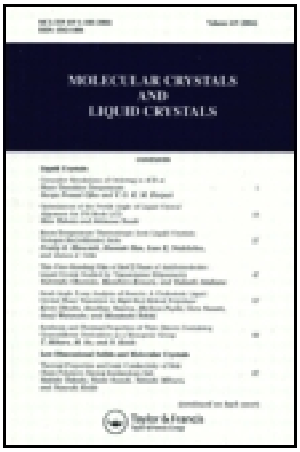

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Syntheses of Model Oligomers for Polyionic Organic Ferromagnetics and their High-Spin Characterization by FT Pulsed Esr/Electron Spin Transient Nutation (Estn) Spectroscopy as a Novel Experimental Technique

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To cite this article: T. Takui, K. Sato, D. Shiomi, S. Nakazawa, M. Yano, T. Kinoshita, K. Abe, K. Itoh, T. Nakamura, T. Momose & T. Shida (1997): Syntheses of Model Oligomers for Polyionic Organic Ferromagnetics and their High-Spin Characterization by FT Pulsed Esr/Electron Spin Transient Nutation (Estn) Spectroscopy as a Novel Experimental Technique, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 363-372

To link to this article: http://dx.doi.org/10.1080/10587259708044588

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 363–372
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SYNTHESES OF MODEL OLIGOMERS FOR POLYIONIC ORGANIC FERROMAGNETICS AND THEIR HIGH-SPIN CHARACTERIZATION BY FT PULSED ESR/ELECTRON SPIN TRANSIENT NUTATION (ESTN) SPECTROSCOPY AS A NOVEL EXPERIMENTAL TECHNIQUE

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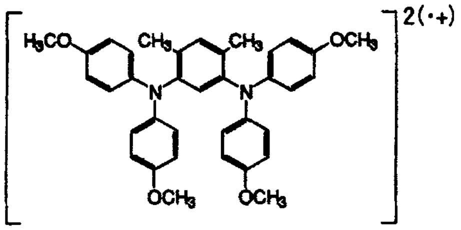
Abstract This paper deals with syntheses and unequivocal spin identification of prototypical model oligomers for the π-topological version of an approach to purely organic polyionic polymer ferromagnets, emphasizing that molecular design exploits the topological super pseudo-degeneracy of π-bonding and π-antibonding molecular orbitals (π-HOMOs and π-LUMOs) appearing close to zero energy in heteroatomic π-conjugated organic systems, for polycationic and polyanionic organic polymeric high spins, respectively. The oxidation and reduction states of the oligomers designed according to the topological approach are expected to undergo dynamic spin polarization, leading to high-spin ground states for both polycationic and polyanionic model oligomers. One-dimensional and two-dimensional star-burst polycationic model oligomers with heteroatoms participating in π-conjugation were designed and synthesized. Their electronic high-spin ground states have been identified by means of Two-Dimensional Electron Spin Transient Nutation (2D-ESTN) spectroscopy based on an FT pulsed ESR technique to which recently we have exerted ourselves in order to obtain technical advances in molecular spin science underlying the research field of molecule-based magnetics. In this study, the polyketone-based polyanionic high-spin species have been generated also by a dry process, *i.e.*, electron doping by γ-irradiation in organic glasses.

INTRODUCTION

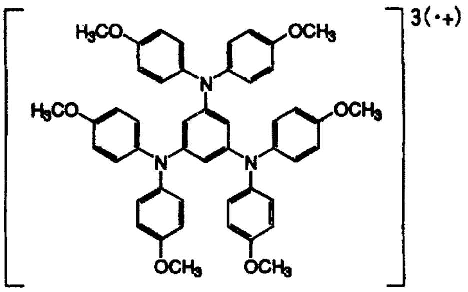
The conceptual proposals of organic magnetics/molecule-based magnetism in terms of non-charged open-shell units were made as early as 1960's, emphasizing that the use of topological-symmetry requirement in the electron network of π-conjugated homoatomic neutral hydrocarbons gives rise to the unlimited degeneracy in non-bonding molecular orbitals (coined as topological degeneracy).[1,2] The last decade has witnessed continuous interest in this interdisciplinary field of organic magnetics/molecule-based magnetics from both the pure and applied sciences.[3-5] The recent rapid development of this field is partly due to the rich variety of novel physical phenomena and properites which synthetic organomagnetic materials are anticipated to exhibit both macroscopically and mesoscopically[3a-c] and partly due to their underlying potential applications[4,5] as future technology in materials science such as spin-manipulated electronics termed as spinics or spintronics.[4] Spinics underlies spin quantum tunneling effects and spin-polarized phenomena appearing on semimacroscopic scale.

Among diverse topics of organic magnetics, pluri-charged high-spin molecular systems generated by the hole or electron doping have recently drawn attention as models for studying the interplay between pluri-charge fluctuation and spin polarization in homoatomic[7,8] and heteroatomic polycationic[9-15] high spin molecular systems as well as in metal-bridged stable polyketone-based polyanionic molecular systems.[16,17] Also theoretically, the doping of organic high-spin systems has been studied referred to molecular design of purely organic magnetic metals and high-Tc organic superconductors, predicting the possible occurrence of the conversion from the low spin states to the high spin states (or vice versa) driven by spin polarization or double exchange mechanisms.[18]

According to our π-topological version of an approach to purely organic polyionic polymer ferromagnets,[19] we have designed the prototypical multi-charged oligomers and synthesized the corresponding diamagnetic precursors, as shown below, in order to illustrate the validity of our approach to polycationic high-spin systems of heteroatomic π-conjugation. Various types of the oligoketone-based polyanionic counterparts have been generated by chemical reduction using alikali-metals. In addition to intramolecular polyanionic high-spin species, metal-bridged molecular high-spin clusters have been identified with the help of the 2D-ESTN spectroscopy. Most of the polyionic high-spin species have been generated by



$\mathbf{1}^{2+}$



$\mathbf{2}^{3+}$

wet processes, *i.e.*, chemical reaction in solution. An attempt has been made to generate oligoketone-basd polyanionic high-spin systems by a dry process, *i.e.*, electron-doping via γ-irradiation in organic glasses.

The ground-state spin structures of the systems at hand have been studied by pulsed FT-ESR/Electron Spin Transient Nutation (ESTN) spectroscopy[20-22] as well as cw ESR spectroscopy. We have developed a two-dimensional version of ESTN spectroscopy which enables us to carry out an unequivocal and facile spin identification generally applicable to non-oriented high-spin systems. The reasons why we have exerted ourselves to develop an ESTN technique are as follows; (1) Multi-charged organic high-spin systems are generated by either electrochemical/chemical oxidation or chemical reduction in solution, giving rise to an ample chance to produce mixtures of low spin states of various levels and overlapping cw ESR spectra. (2) With increasing spin quantum number *S*, spectral densities near g = 2 region in fine-structure ESR spectra from random orientation increase enormously, spectral simulation failing when various *S*'s contribute to the spectra. Thus, a novel spectroscopic methodology is required for the spectroscopic resolution enhancement enabling us to unequivocally discriminate between electron spin multiplicities in spin mixtures. The appearance of the overlapping spectra is rather intrinsic to high spin systems of π-conjugation, intra- or inter-molecular high spins, in which two-center π-π spin interactions dominate. The ESTN technique is only briefly described in the experimental section of this paper and the details has been published elsewhere.[22] Two-dimensional field-swept ESTN (2D-ESTN) spectroscopy is presented in order to illustrate the powerfulness and experimental feasibility of this novel ESR technique. From the methodological viewpoint the 2D-ESTN spectroscopy is totally different from conventional cw-ESR spectroscopy.

THEORETICAL; PULSED FT-ESR/ESTN SPECTROSCOPY

ESTN spectroscopy is based on electron spin resonance to measure the spin Hamiltonian in terms of the rotating frame. In terms of a classical vectorial picture for the motion of the spin magnetization $\boldsymbol{M_0}$ in the presence of static magnetic field $\boldsymbol{B_0}$ presseses at the nutation angle ϕ with nutation angular frequency $\omega_n = \gamma \boldsymbol{B_e}$ from the initial direction around the effective field $\boldsymbol{B_e}$ by applying microwave field ($\boldsymbol{B_1}$) pulse with the width t_1. The nutation frequencies are dependent on an ESR transition involved, *i.e.*, a spin quantum number *S*, and M_S-manifold, as well as a ratio (ω_D/ω_1) of a zerofield splitting parameter (ω_D) and strength of the microwave radiation field ($\omega_1 = \gamma \boldsymbol{B_1}$).

The quantum mechanical description of the nutation phenomena in pulse experiments

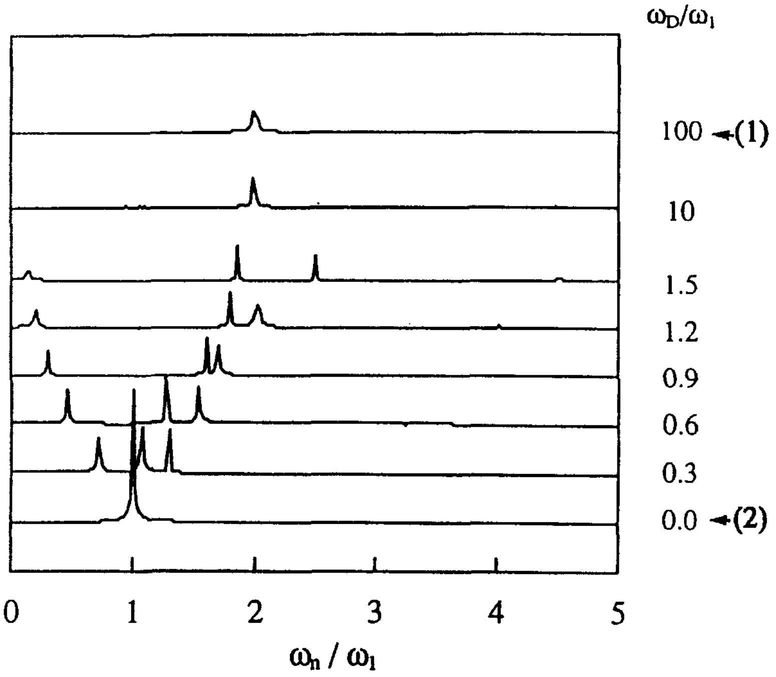


FIGURE 1. Dependence of the nutation frequency ω_n on the ratio ω_D/ω_l.

invokes the equation of the motion of the density matrix governed by the Liouville-von Neumann equation.[22] The induction signal by the precessing magnetization of the spin system is expressed in proportion to

$$\langle S(t)\rangle = \sum\langle M_s - 1|\,\rho(0)\,|M_s\rangle[S(S+1) - M_s(M_s - 1)]^{1/2}$$
$$\times \exp\{it\omega_D(2M_s - 1) + \omega_l t[S(S+1) - M_s(M_s - 1)]^{1/2}\},$$

where the summation runs over M_s and only the ω_D term in fine-structure spin Hamiltonian remains in the first order approximation. Thus, in the weak extreme limit of the microwave radiation field, *i.e.*, $\omega_D/\omega_l \gg 1$, the nutation frequency ω_n for an $M_s \Leftrightarrow M_s - 1$ ESR allowed transition is given by a simplified equation as follows;

$$\omega_n = \omega_l\,[S(S+1) - M_s(M_s - 1)]^{1/2}.$$

The nutation frequency depends on S and M_s as well as ω_l which is proportional to the effective microwave field strength on the sample site. Note that this weak limit condition is satisfied under ordinary experimental conditions whenever the zerofield splitting parameter ω_D is larger than 10^{-3} cm^{-1}.

Figure 1 exemplifies the nutation frequency dependence on the ratio for a transition $M_s = 1/2 \Leftrightarrow M_s = -1/2$ of $S = 3/2$. In the weak extreme limit, the ratio ω_D/ω_l for $S = 3/2$ is equal to 2 according to the above simplified equation, as shown by an arrow (1) in Figure 1. Experimentally, this has been demonstrated for Cr^{3+} in MgO.[22] It has turned out that the well-known vanishing fine-structure constant for Cr^{3+} in MgO is not correct and shows an appreciable amount of symmetry reduction around the Cr^{3+} site.

EXPERIMENTAL

2D-ESTN Spectroscopy

The nutation experiment can be made by either observing the FID or electron spin echo (ESE) signal $s(t_1, t_2)$ as time domain spectroscopy by incrementing the time interval t_1 of microwave pulse excitation parametrically. Figure 2 shows a schematic timing diagram for ESE-detected nutation experiments. The two time variables t_1 and t_2 are independent. $s(t_1, t_2)$ measured as a function of t_1 and t_2 is converted into a 1D or 2D frequency domain spectrum, *i.e.*, $S(f_1, t_2)$ (or $S(t_1, f_2)$) or $S(f_1, f_2)$ by Fourier transformation. $S(f_1, t_2)$ gives the 1D nutation spectrum at a given static magnetic field $\boldsymbol{B_0}$. Thus, $\boldsymbol{B_0}$-swept nutation spectra can be obtained in a 2D representation, yielding spectroscopic resolution enhancements and unequivocal *S*-discrimination in frequency-domain field-swept 2D spectra from spin mixtures. In the field-swept 2D spectroscopy applied to non-oriented systems, all the orientations of the systems contribute to the corresponding nutation frequency spectra. In order to reconstruct complete nutation-frequency spectra, contributions from the orientations giving rise to the resonance field are evaluated. The field-swept 2D presentation is of essential importance in the ESTN spectroscopy for non-oriented high-spin systems, as described below. This novel technique is applicable also to open-shell systems with exchange narrowing lines by the use of an FID detection scheme.[22] In this study, ESTN measurements were made by an ESE detection scheme composed of a three pulse sequence, as shown in Figure 2, simply because of the occurrence of inhomogeneously broadened cw-ESR lines in organic glasses. The ESTN spectroscopy is essentially free from spectral simulation required for randomly oriented systems in order to identify S and M_s values of high spin systems.

Materials

During the course of model studies of polyionic high-spin oligomers, a series of 1,3-bis(diarylamino)benzenes and 1,3,5-tris(diarylamino)benzenes and their analogues have been adopted for precursors of polycationic high-spin systems. They were synthesized via a sequence of Ullman coupling reactions. 1,3,5-Tris(diarylamino)benzenes were synthesized

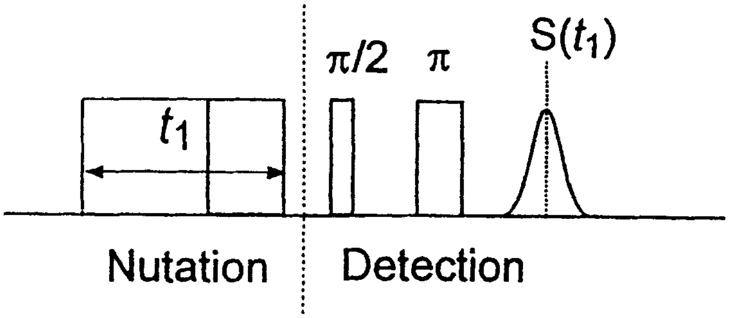


FIGURE 2. Schematic timing diagram for ESE-detected transient nutation experiments.

following the reported method. Also, a series of *meta*-, 1,3,5-polyketones and heteroaromatic polyketones have been synthesized for precursors of polyanionic high-spin model oligomers. Their ground-state spin multiplicities of the oxidized or reduced states have been for the first time identified by ESTN spectroscopy applied to randomly oriented high-spin systems in organic rigid glasses, as exemplified below.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 3 exemplifies a B_0-swept 2D nutation spectrum of *N, N, N', N', N'', N''*-hexa(4-anisyl)-1,3,5-triaminobenzene trication 2^{3+} [10, 11] observed at 6 K in dichrolomethane under the experimental condition of the weak extreme limit. The projection onto the magnetic field axis gives a B_0-swept ESR spectrum where a and c, and b designate the $M_s = \pm 3/2 \leftrightarrow \pm 1/2$ and $M_s = 1/2 \leftrightarrow -1/2$ ESR allowed transition for $S = 3/2$, respectively. The nutation frequency corresponding to a and c appears at the peaks of 8.12 MHz in the 2D contour plot, while the frequency to c at a single peak of 10.08 MHz, the ratio 10.08/8.12 being in good agreement with the theoretical value $2/3^{1/2}$ given by the above equation. Under the experimental condition the nutation frequency ω_n corresponding to $S = 1/2$ species was 5 MHz and no trace peak was observed at 6 K, as shown in Figure 6. Thus, it is unequivocally concluded that the ground state of 2^{3+} is spin-quartet and excited doublet states are located higher than 300 cm^{-1} above the ground state from the temperature dependence of the nutation spectra. These findings agree with the theoretical expectation for the spin structure of the model polycationic high-spin oligomers. The 2D spectra in Figure 3 also shows that 2^{3+} is stabilized by *p*-methoxy substitution and there is no contamination from spin-doublet

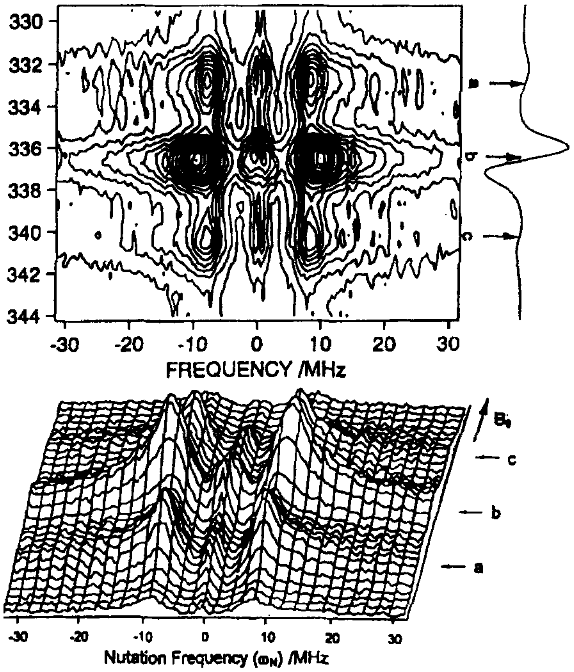


FIGURE 3. Magnetic field B_0-swept 2D nutation spectrum of 2^{3+} observed at 6 K.

species of by-products during the chemical reaction.

In order to obtain intramolecular polyanionic high-spin species originating in polyketones, concentration and reaction-temperature controlled experiments were carried out, while intermolecular high-spin clusters of $S = 1$, 3/2, and 2 have dominated in the observed spectra from the chemical reduction of 1,3-dibenzoylbenzenes in solution. All the identified fine-structure constant related values $(2S - 1)|D|$ obtained for reduction states under study fall in the range as small as 1.2×10^{-2} cm^{-1} and they depend on alkali-metals used in the chemical reduction, indicating that these arise from metal bridge-based intermolecular high-spin clusters in the ground state. Semiempirically estimated values $(2S - 1)|D|$ for intramolecular polyanionic high-spin species under study range from three times to four times of 1.2×10^{-2} cm^{-1}, depending on their molecular structures. It is essential to characterize the spin structure of typical intramolecular polyanionic high-spin species in order to interpret frequently occurring intermolecular high-spin clustering.[17] The 2D-ESTN experiments on the diketone-based anionic systems showed direct evidence for intermolecular tri- and tetra-anionic dimers with $S = 3/2$ and 2 in the ground state, respectively, indicating the generation of intramolecular dianionic high-spin species which are attributable to the diketone-based dianions of $S = 1$. Semiempirical based calculations for zerofield splitting tensors of the intermolecular dimers are under way.

The quest for stabilized polyketone-based or other polyanionic high-spin systems is the focus of current topics in this field. It has turned out during the present study that the introduction of heteroaromatic ring stabilizes the polyanionic systems enormously.

Metal free polyketone-basd polyanionic high-spin clusters have been for the first time identified which have been generated by a dry process, *i.e.*, thermal electron attachment via γ-irradiation in 2-methyltetrahydrofuran glasses. The observed D values are larger than those of the corresponding intermolecular clusters obtained by alkali-metallic reduction, providing a clue to molecular conformations at binding sites.

A VB approach in terms of molecular orbital and band structure calculations has been invoked in order to expound charge fluctuation vs. dynamic spin polarization in topologically controlled polyionic high-spin systems of simplified molecular structures.[23] The approach is π-electron based, the simplest and does not consider the corresponding counter ions. It has turned out that the approach gives significant physical pictures for organic systems with multi-charges and multi-parallel spins. Details will be described elsewhere.

CONCLUSION

π-Topologically controlled polycationic and polyanionic high-spin oligomers in their ground state have been studied as models for organic magnetic metals. The model oligomers have been synthesized and their ground-state spin multiplicities have been unequivocally identified by pulsed ESR/2D-ESTN spectroscopy applied to randomly oriented high-spin systems.

The molecular design has invoked the use of topologically 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. As far as robust spin polarization takes place in the topological electron network of heteroatomic π-conjugation, the highest spin multiplicity can be predicted. Otherwise, low spin ground states can occur particularly for polycationic cases. All the experimetal data in this work provided evidence of the above theoretical expectation

Intermolecular polyanionic high-spin clusters from oligoketones have been generated by the dry process of γ-irradiation in organic glasses. These clusters exemplify metal-bridge free intermolecular polyanionic high-spin organic systems.

Magnetic Field-swept 2D-ESTN spectroscopy applied to high spin mixtures in non-oriented media is straightforward and feasible to discriminate between high spins of different spin multiplicities.

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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