

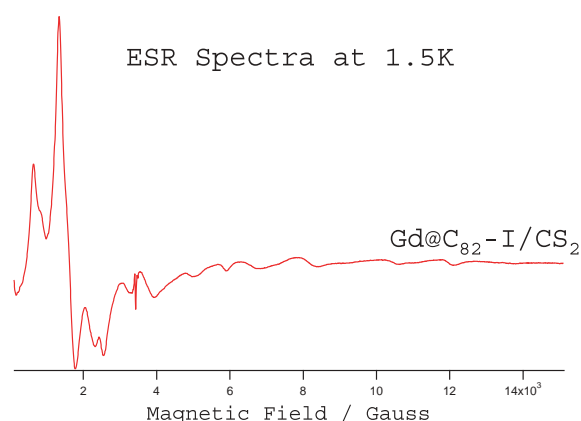
## II-H Molecular and Electronic Structures of Metallofullerenes

The continued interest in radical ions of fullerenes and metallofullerenes has resulted from the discovery of superconductivity in the CT complexes of alkali metals with fullerenes. Spectroscopic information concerning the electronic and spin states of the metallofullerenes has been obtained by cw- and pulsed-EPR measurements.

### II-H-1 High-Field/High-Frequency ESR Study of Gd@C<sub>82</sub>

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The X-band ESR investigations of La@C<sub>82</sub>, Y@C<sub>82</sub>, and Sc@C<sub>82</sub> have been reported. In these metallofullerenes, the electronic structures of the metal atoms are described as  $nd^{1(n+1)}s^2$ . They have been reported that these metallofullerenes have the doublet ground states originating in the organic  $\pi$  radical of the C<sub>82</sub> trianion via the electron transfer from metal atoms to C<sub>82</sub> cage. On the other hand, the electronic structure for Gd atom is described as  $4f^75d^16s^2$ , and the ground high-spin state is expected. Our purpose in this work is the examination of the spin state of Gd@C<sub>82</sub> and of the cage effect of the fullerene C<sub>82</sub>. Highly purified Gd@C<sub>82</sub> was obtained by high performance liquid chromatographic (HPLC) method. We examined Gd@C<sub>82</sub> in CS<sub>2</sub> solutions in terms of X- and W-band ESR spectroscopy. Figure 1 shows the X-band ESR spectrum for Gd@C<sub>82</sub> in CS<sub>2</sub> solution at 1.5 K. The spectrum pattern corresponds to that for the high-spin systems with large fine structure. The unsymmetrical spectral feature was given because of the large zero-field splitting parameter  $D$  and  $E$ , and prevented us from an easy spectral simulation. The W-band ESR measurement was performed to simplify the spectrum of Gd@C<sub>82</sub>.



**Figure 1.** The X-band ESR spectrum for Gd@C<sub>82</sub> in CS<sub>2</sub> solution at 1.5 K.

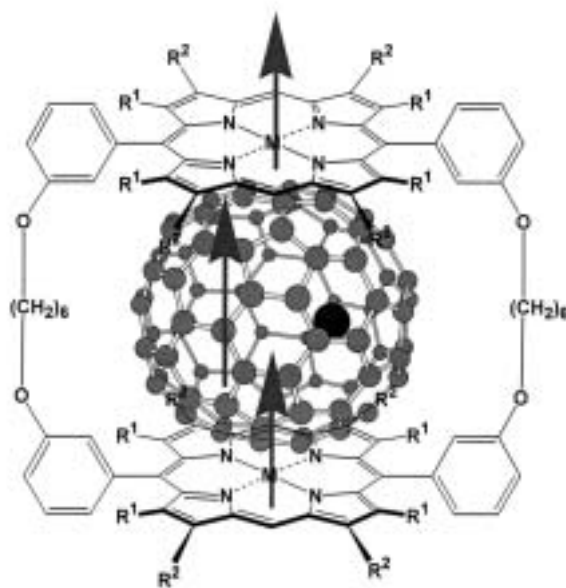
### II-H-2 Spin State of an Inclusion Complex of a Cyclic Dimer of Metalloporphyrin with La@C<sub>82</sub>

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A paramagnetic metallofullerene is a nice building block for a molecular magnet. Wrapping of a metallofullerene with larger  $\pi$ -conjugated molecular envelopes is of great interest, which may lead to an extension of the super-molecular magnet in a 3D-fashion. Tokyo group of authors has synthesized a cyclic dimer of metalloporphyrin,<sup>1)</sup> as shown in the figure, and reported the big association constant of  $6.7 \times 10^5 \text{ M}^{-1}$  for the inclusion complex of a cyclic dimer of zinc porphyrin with C<sub>60</sub> in benzene solution. The big association properties would come from the flexibility of linkers between two porphyrins. The hexamethylene linkers of the dimer were folded to adjust the porphyrin-porphyrin distance, and the porphyrin macrocycles were slightly distorted from the planar structure so as to fit the shape of C<sub>60</sub>. The electron spin state of an inclusion complex of a cyclic dimer of metalloporphyrin with metallofullerene was investigated by means of pulsed electron spin resonance (ESR) measurement. The direct experimental evidence of the coupled spin state of  $S = 3/2$  was obtained for the cyclic dimer of copper-porphyrin with La@C<sub>82</sub> by the nutation measurement of pulsed ESR. A big variety would be expected for the spin state of the inclusion complex in terms of the combination of metals on a porphyrin and a fullerene.

#### Reference

- 1) K. Tashiro, T. Aida, J.-Y. Zheng, K. Kinbara, K. Saigo, S. Sakamoto and K. Yamaguchi, *J. Am. Chem. Soc.* **121**, 9477 (1999).



**Figure 1.** Molecular model of an inclusion complex of a cyclic dimer of metalloporphyrin with metallofullerene La@C<sub>82</sub>.

## II-I High Field and Pulsed Electron Spin Resonance Spectroscopy

Electron spin resonance (ESR) spectroscopy has been a powerful technique for the characterization of radical species. The modern development of EPR spectroscopy enables us to investigate the heterogeneous and disordered system in detail. Especially the high frequency and pulsed EPR methods achieve the substantial resolution enhancement of spectrum. The advanced EPR spectroscopy is applied to study on the reaction mechanism in the heterogeneous system and the detection of the dication species.

### II-I-1 Radical Products in Mechanochemical Dechlorination of Hazardous Organochlorine on CaO Surface

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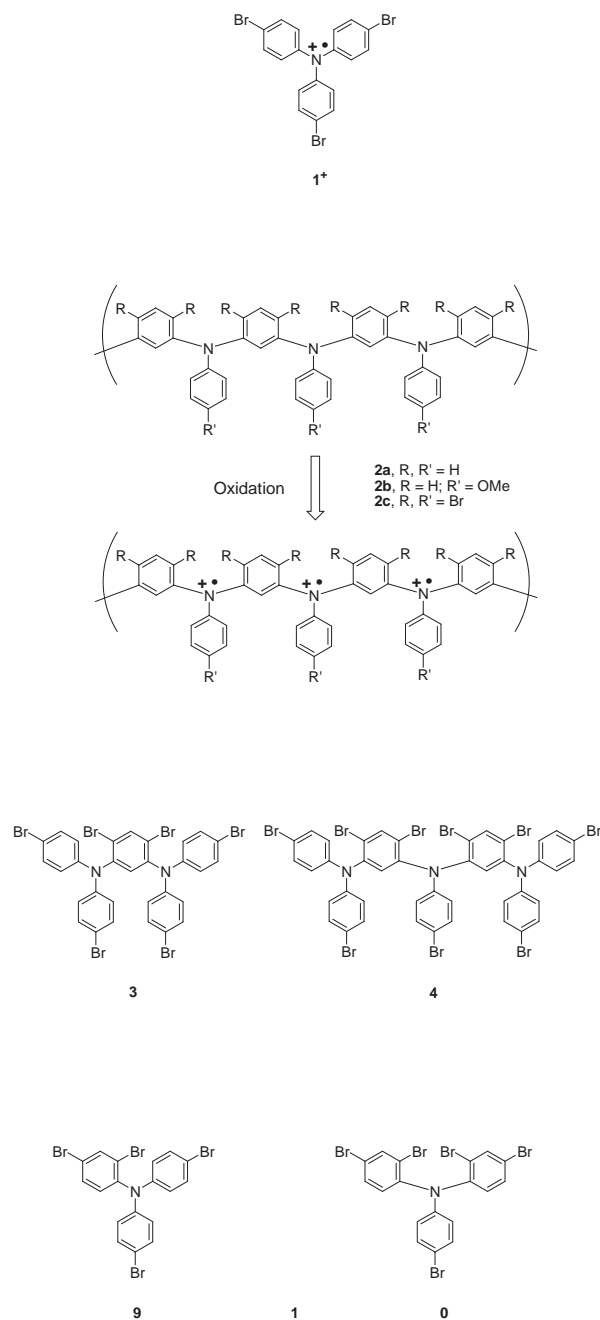
It is widely recognized that hazardous chlorinated organic compounds such as poly-chloro-dibenzoparaoxin (dioxin), poly-chloro-benzofuran and coplanar poly-chloro-biphenyl (PCB) are the most dangerous pollutants to our environment and health. Such great concern has led to many investigations for the complete decomposition of these toxic compounds. Recently mechanochemical method with alkaline earth metals (Mg, Ca) or their oxides have attracted attention as a practically simple and useful process to degrade chlorinated organic compounds. It is, therefore, desired to investigate the reaction mechanism of the mechanochemical dechlorination that is a solid state reaction. The advanced EPR spectroscopy is applied to study the reaction mechanism in the mechanochemical dechlorination of organochlorine using inorganic reactants. For the first time, we detected the paramagnetic products created by grinding 3-chlorobiphenyl (BP-Cl) with calcium oxide (CaO) as reactant in a ball mill, which is one of the promising ways to detoxify hazardous chlorinated organic compounds. Those products were attributed to phenoxy radicals coming from BP-Cl and trapped electrons in oxygen vacancies on the reactant surface by using high frequency and pulsed electron paramagnetic resonance spectroscopies. A radical mechanism for the destruction of organochlorine was proposed, since the good correlation between the dechlorination efficiency and the radical yield were observed. The mechanical stressing may induce the electron transfer from O<sup>2-</sup> site on the surface of CaO to organic compounds and the produced organic anion radicals undergo an effective self-dissociation of the chlorine-carbon bond.

### II-I-2 Facile Synthesis, Crystal Structures, and High-Spin Cationic States of All-*para*-brominated Oligo(*N*-phenyl-*m*-aniline)s

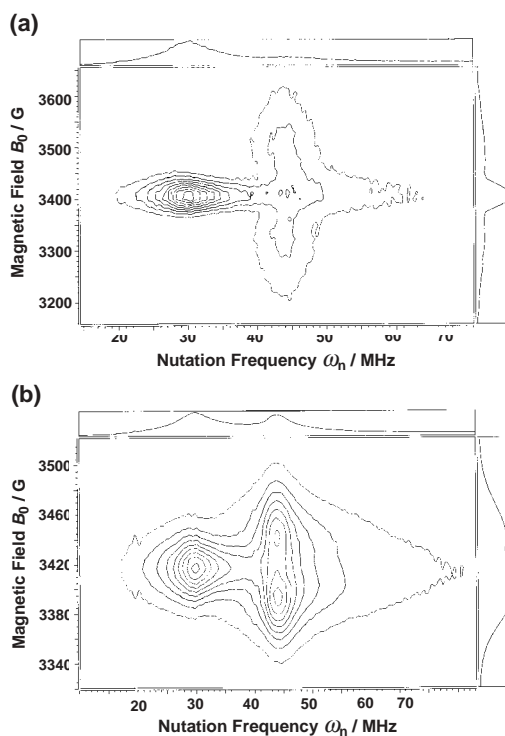
KANEMOTO, Katsuichi; KATO, Tatsuhisa; ITO, Akihiro<sup>1</sup>; INO, Haruhiro<sup>1</sup>; TANAKA, Kazuyoshi<sup>1</sup>

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Syntheses of both the dimer (**3**) and the trimer (**4**) of all-*para*-brominated poly(*N*-phenyl-*m*-aniline)s (**2c**) were achieved in a one-pot procedure from the parent non-brominated oligomers and benzyltrimethylammonium tribromide (BTMA-Br<sub>3</sub>), see Scheme 1. An X-ray crystallographic analysis revealed that **4** has a U-shaped structure, suggesting that **2c** easily adopts helical structures. Furthermore, the redox properties were investigated by the UV-vis and EPR measurements. It was confirmed that the both **3** and **4** can be oxidized into the dications **3**<sup>2+</sup> and **4**<sup>2+</sup> with triplet spin-multiplicity. In order to identify the spin multiplicity of this species, we adopted the pulsed EPR method based on the fact that the magnetic moments with distinct spin quantum numbers (*S*) precess with their specific nutation frequency ( $\omega_n$ ) in the presence of a microwave irradiation field (*B*<sub>1</sub>) and a static magnetic field (*B*<sub>0</sub>). Figure 1 shows the relation between the EPR spectra observed at 5 K and its transient nutation spectra in a 2-D contour representation. Namely, the projection on the magnetic field axis corresponds to the usual EPR spectrum, while the projection on the frequency axis to the nutation spectrum. The intense peak observed at 3410 G (3415 G) is expected to be  $|1/2, +1/2\rangle \leftrightarrow |1/2, -1/2\rangle$  transition of the doublet species **3**<sup>+</sup> (**4**<sup>+</sup>) and had the nutation frequency of 30.0 MHz (30.0 MHz), indicating  $\omega_1 = 30$  MHz. On the other hand, two peaks at 3325 and 3510 G (3395 and 3445 G) had the same nutation frequency of 43.8 MHz (43.9 MHz), suggesting the presence of a high-spin cationic species of **3** (**4**). Here, the frequency ratio ( $\omega_n/\omega_1$ ) of 43.8/30.0 (43.9/30.0) is in good agreement with the ratio of  $\sqrt{2}$  expected for  $|1, 0\rangle \leftrightarrow |1, \pm 1\rangle$  transition of the triplet state. As a result, the high-spin species generated by excess of SbCl<sub>5</sub> can be regarded as **3**<sup>2+</sup> (**4**<sup>2+</sup>).



Scheme 1. Molecular structures of aromatic amines.



**Figure 1.** Field-swept electron spin nutation spectra of (a) **3** and (b) **4** oxidized by excess  $SbCl_5$  in  $CH_2Cl_2$  at 5 K.  $\omega_1$  corresponds to 30 MHz.

## II-J State Correlated Raman Spectroscopy

The vibrational Raman polarizability tensor responds to molecular reorientational relaxation process, and the structural environment in condensed media. The measurement of Raman scattering is a powerful technique for the study of molecular motion and of the mechanism of phase transition. We've built up the system of multichannel type detection of Raman scattering combined with the temperature controlled cell.

## II-J-1 Probable Langevin-Like Director Reorientation in an Interface-Induced Disordered $SmC^*$ -Like State of Liquid Crystals Characterized by Frustration between Ferro- and Antiferroelectricity

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To clarify the thresholdless, hysteresis free V-shaped switching due to frustration between ferro- and antiferroelectricity, we have studied a prototype binary mixture system. The apparent orientational order parameters,  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$ , obtained from polarized Raman scattering in thin homogeneous cells indicate that substrate interfaces induce some randomization of local in-plane directors at the tip of the V. Their correlation length,  $\xi_{\parallel} \approx 3.5$  nm and  $\xi_{\perp} \approx 75$  nm, have been estimated by assuming the Langevin-like reorientation. Because of the much shorter  $\xi_{\parallel}$  and  $\xi_{\perp}$  than the visible light wavelength, the switching process looks uniform.

## II-J-2 Orientational Distributions in Smectic Liquid Crystals Showing V-Shaped Switching Investigated by Polarized Raman Scattering

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The polarized Raman scattering of two types of liquid crystals showing the thresholdless, hysteresis-free V-shaped electro-optic response in thin homogeneous cells was measured in the temperature range of antiferroelectric smectic phase. One sample was one component of Inui mixture [compound **a** in the Figure 1(A)] and the other was so-called Mitsui mixture [Figure 1(B)]. The apparent orientational order parameters,  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  were evaluated for the C–C stretching mode of phenyl ring. The obtained order parameters at the tip of the V-shaped switching were  $\langle P_2 \rangle = 0.70$  and  $\langle P_4 \rangle = 0.35$  for the compound **a**,  $\langle P_2 \rangle = 0.59$  and  $\langle P_4 \rangle = 0.20$  for the Mitsui mixture. The model calculations confirmed two extreme distribution of the local in-plane director at the tip of the V. The compound **a** exhibited a small distribution, while the Mitsui mixture did a very large distribution. The difference in the distribution of two types of liquid crystals at the tip of the V was explained by the barrier between synclinal and anticlinal ordering in adjacent layers. The small barrier gave a large distribution at the tip of the V in the dynamic switching, consequently triggered the V-shaped switching even in the first run. On the other hand, the large barrier did a small distribution and the tristable switching.

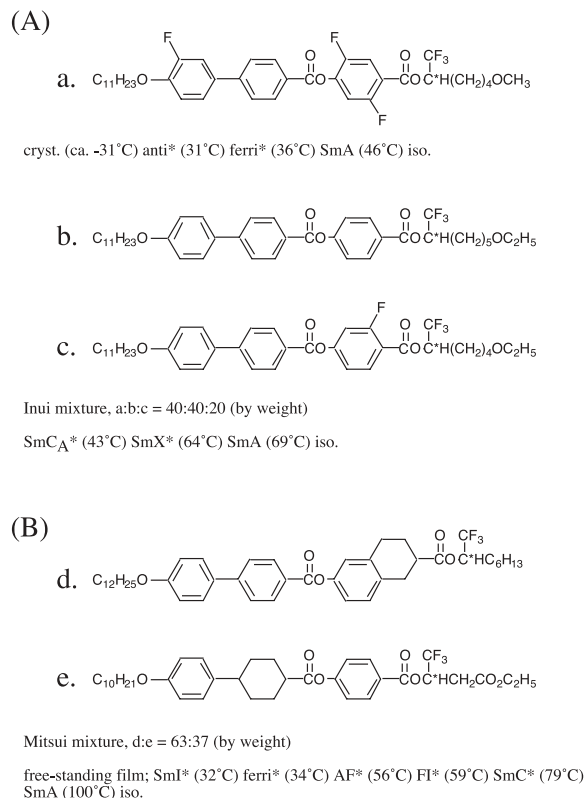


Figure 1. The Inui mixture (A) and the Mitsui mixture (B).