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Electron Spin Resonance Studies of Organic Electronic Materials and Devices

Shin-ichi Kuroda

Overview

Organic electronics is regarded as one of the key technologies that may bring innovation to electronics in the 21st century. Organic electronic devices such as electroluminescent (EL) displays, field-effect transistors and solar cells attract much attention as low-cost devices with flexibility. Varieties of organic semiconducting materials based on π -conjugated polymers and small molecules have been synthesized since the discovery of the conducting polymer polyacetylene by Shikarawa, Heeger and MacDiarmid. Unpaired electrons in these materials such as solitons and polarons carry spin and charge and play important roles in exhibiting the functions of materials. Based on this understanding, the author has been engaged in the application of electron spin resonance (ESR) spectroscopy as a powerful microscopic tool to investigate the fundamental properties of organic electronic materials and the electronic processes in the devices by detecting the unpaired electron spin.

Initial challenge was the studies of the nanoscale spatial extent of solitons and polarons in conducting polymers. In particular, soliton in polyacetylene was the most fundamental problem. By employing electron-nuclear double-resonance (ENDOR) technique, that can determine the hyperfine coupling between the unpaired electron spin and nearby protons in a high accuracy, soliton extension close to the theoretical prediction was successfully observed, providing strong evidence for their existence. Use of stretch-oriented samples was essential in confirming the anisotropic properties of π -electron that played crucial role in the ESR and ENDOR analysis. The next problem was the ENDOR studies of polarons in the first EL polymer PPV, discovered by R. Friend, which also provided the first example of the confirmation of polaron extension in conducting polymers.

Studies of EL polymers opened up a new study of optically-generated polarons by using light-induced ESR (LESR) measurements. The method was further extended to the conducting polymer/fullerene composites and light-induced ENDOR (LENDOR) technique was also successfully applied. Eventually, organic transistors of high-mobility polymers such as regioregular polythiophene (RR-P3HT) attracted considerable attention. While direct observation of charges in organic devices remained a big challenge, various optical methods were already introduced to such purpose but no spin detection. This motivated us to develop a completely new ESR method, field-induced ESR (FI-ESR) method which can detect spins of the charges injected at the interface of organic transistors. First, the method

was applied to the polymer then to typical high-mobility small molecule pentacene and others. The method has proved to be useful in clarifying electronic states, spin-charge relation, wave functions, dynamics, and local molecular orientations, crucial for device performance. In the following, the main results of those ESR researches on π -conjugated polymers and small molecular organic semiconductor materials and devices are reviewed.

1. ENDOR studies of soliton in polyacetylene

Polyacetylene attracted much attention not only due to its metallic conductivity upon doping, but also for the soliton predicted as the nonlinear excitations in one-dimensional electron system. The soliton in polyacetylene is a bond alternation kink where the single-double bond alternation order is reversed by the soliton, resulting in the kink structure with two successive single bonds and one unpaired electron that can be detected by ESR (Fig. 1(a)). The unpaired electron was predicted to be delocalized on the conjugated chain, and the observation of its extension was one of the key problems in providing evidence for its existence. The author proposed that ENDOR is a suitable method to observe the shape of soliton, by the determination of the hyperfine coupling between the unpaired electron spin and nearby protons on the conjugated chain, that can provide the spin distribution of the soliton.

Prior to the ENDOR studies, an important prerequisite was the confirmation of the π -electron character of the unpaired electron as predicted from the molecular structure of the soliton. Theory of the hyperfine coupling of π -electron has to be used to in the ENDOR analysis. There were certainly the unpaired electrons observed in the polymer and they also exhibited the motional effect as predicted from the theory, however, there were no direct confirmation of π -electron character. The author pointed that since π -electron exhibits characteristic anisotropy in the ESR parameters such as g - and hyperfine coupling tensors, it should be reflected on the ESR spectra if we use stretch-oriented samples. Indeed such π -electron character has been observed in stretch-oriented Shirakawa polyacetylene, in the anisotropy of ESR g -values and hyperfine-determined linewidth, confirming that the unpaired electrons in polyacetylene are π -electrons. Since then, the anisotropic properties of g and hyperfine coupling have been playing key roles in the analysis of physical properties such as molecular orientations in organic thin films and devices of π -conjugated systems. The research in polyacetylene has provided the starting example of such analysis.

ENDOR spectra were successfully observed down to 4K using stretch-oriented samples, and the spectral line shape directly provides the detail of soliton spin distribution (Fig. 1(d)) [1,2]. From the maximum ENDOR shift, the peak spin density $\rho(0)$ at the center of the soliton is obtained. Another important feature is the existence of the distinct spectral turning

point for the spectra of parallel direction, which provides direct evidence of the existence of the second group of spin density, that is negative spin sites arising from the electron correlation effect. Thus determined spin density extends over about 18 carbon sites in half width and the detailed profile was well reproduced by the theory incorporating the effect of electron correlation (Fig. 1(e)). After our work, similar spin distribution was reported by the ENDOR using stretch-oriented polyacetylene samples prepared by the method different from Shirakawa method. From these results together with evidence of other predicted properties, now the existence of the soliton in polyacetylene is well established.

Confirmation of the existence of soliton in polyacetylene has significant meaning in that the model Hamiltonian predicted soliton is essentially correct in describing the properties of conducting polymers, supplemented with electron correlation effect, and it thus keeps providing a basic tool to describe the properties of π -conjugated systems used in organic electronics. More specifically, since the majority of charge carrier, polaron in conjugated polymers is physically the soliton pair (one is neutral and the other is charged), soliton provides the basis for understanding the optoelectronic properties of polymeric devices.

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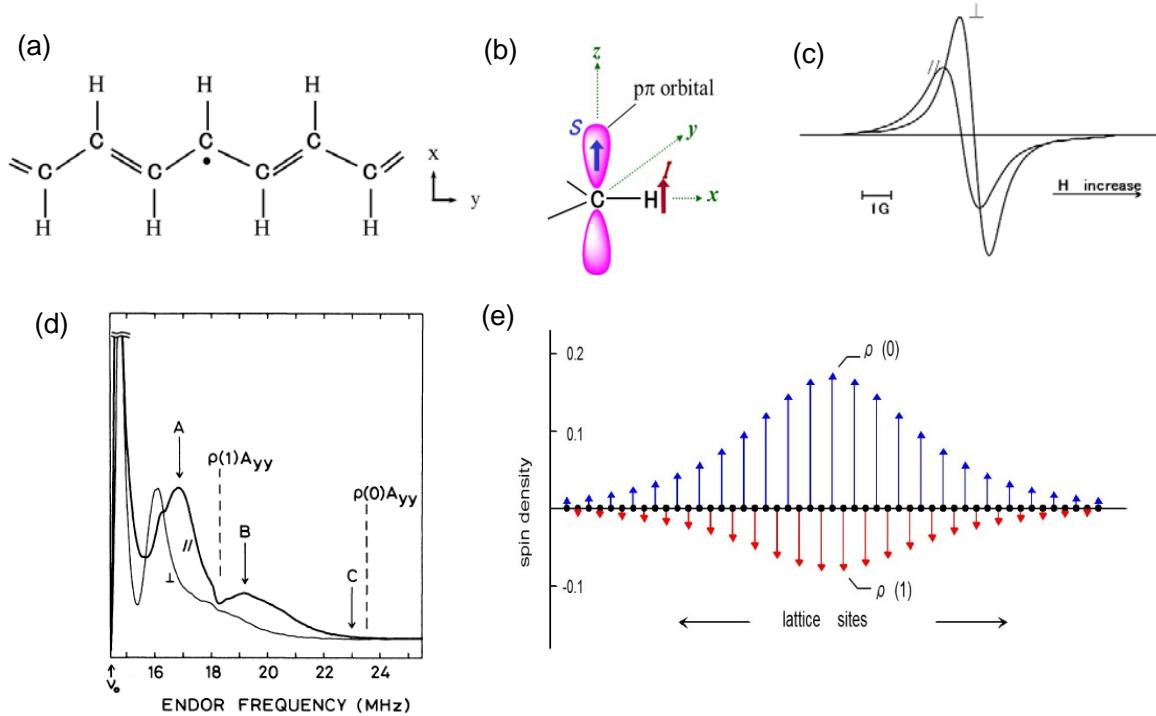


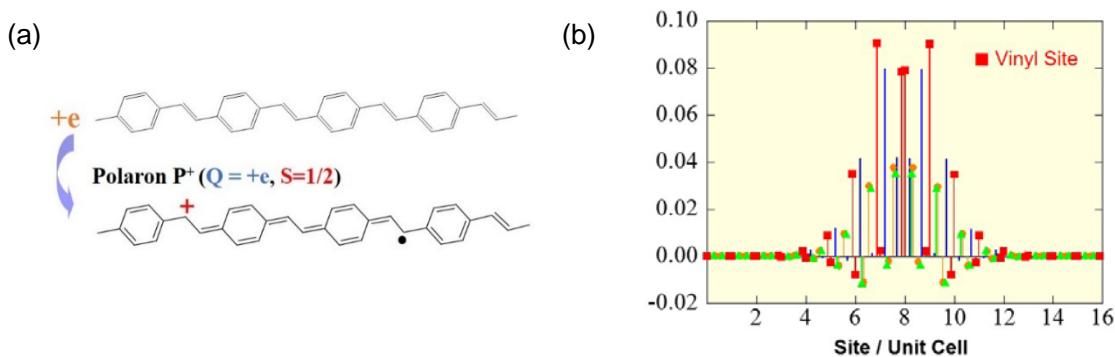
Fig. 1 (a) Soliton in polyacetylene. (b) p π orbital of a carbon atom. (c) Anisotropic ESR signals in stretch-oriented polyacetylene film. (d) ENDOR spectra in stretch-oriented polyacetylene²⁾. (e) Spin density distribution of soliton.

2. ENDOR studies of polaron in conjugated electroluminescent polymer, poly(paraphenylene vinylene) and light-induced ESR

After the discovery of metallic conductivity in polyacetylene and other polymers, another outstanding property was added to conjugated conducting polymers. That is, intense electroluminescence was discovered in poly(paraphenylene vinylene) (PPV). Electroluminescence occurs from the recombination of positive and negative carriers injected from the electrodes of the device and hence their studies are of fundamental importance. The charge carrier, polaron, is shown in PPV structure in Fig. 2(a). When we dope the neutral polymer, polaron as a soltion pair (one is neutral and the other is charged) is created and it has spin 1/2 and charge $+e$ and can be detected by ESR. Using stretch-oriented samples, ENDOR spectra of polarons in PPV have been successfully observed [1]. The observed spectra were well reproduced by the theory. The results revealed that the polaron extension of about 4 phenyl rings with the maximum spin density residing on the vinyl sites (Fig. 2(b)) [2]. The polaron spin distribution thus observed provided evidence for their existence.

Eventually, soluble derivatives of PPV polymer were developed for which we have carried out LESR experiments. Comparison of LESR spectra of PPV derivatives with different molecular structures enables us to obtain prominent results, that is, site-selective information of electron distribution in PPV backbone structure [3]. According to our ENDOR analysis, the major electron density resides on the vinyl sites. Comparison of LESR spectra between CN-PPV where a proton on the vinyl sites is substituted by a CN group without proton and MEH-PPV, clear decrease of hyperfine-determined LESR linewidth in CN-PPV was observed due to the loss of the proton (Fig. 2(d)). The results were quantitatively reproduced by the theoretical spin distribution obtained by ENDOR analysis and gives further evidence of the validity of ENDOR study supplemented by LESR study.

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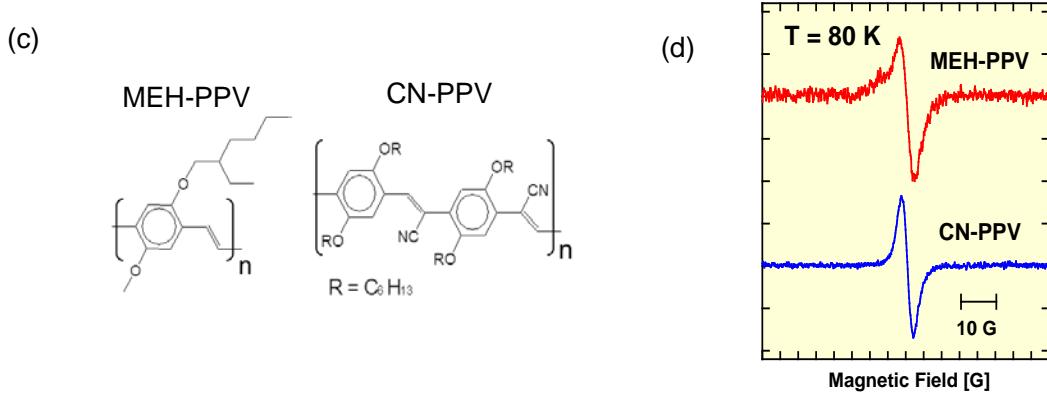


Fig. 2 (a) Polaron in an electroluminescent polymer PPV. (b) Theoretical spin distribution of polaron in PPV²⁾. (c) Molecular structure of MEH-PPV and CN-PPV. (d) LESR spectra of MEH-PPV and CN-PPV³⁾.

3. LESR and LENDOR studies of conjugated polymer/fullerene composites

Regioregular poly(3-hexyl thiophene) (RR-P3HT) is a prototypical high mobility polymer with regular attachment of alkyl chains that results in the formation of crystalline lamellar structure on the substrate. Due to this crystallinity field-effect mobility reaches high value of $\sim 0.1 \text{ cm}^2/\text{Vs}$. Composites with fullerene become solar cell materials. Composites of conjugated conducting polymer with fullerene exhibit highly efficient photoinduced charge transfer (CT) suitable for solar cell materials. Due to this CT, LESR studies become possible, however, no previous LESR existed in the case of RR-P3HT/C₆₀ (Fig. 3(a)) and we have reported the first LESR signals [1]. We further measured LENDOR (Fig. 3(b)) and succeeded in observing the spatial extent of wave functions of positive polaron of P3HT corresponding to polaron half width of about 10 thiophene rings [2].

Furthermore, by observing the excitation light power dependence of LESR signals (Fig. 3(c)), we have discovered novel quadrimolecular recombination process that involves the simultaneous recombination of two positive and two negative charge carriers, instead of usual bimolecular recombination. Contribution of two positive charges strongly suggests the formation of bipolarons (or polaron pairs) in the intermediate process of charge recombination. Besides P3HT, we also succeeded in LESR and LENDOR measurements of composites of fullerene with a blue-light emitting polymer, polyfluorene (PFO) [3]. LENDOR results showed that the half width of the polaron spin distribution in PFO was three PFO monomer units. In LESR, bimolecular recombination process was observed instead of quadrimolecular recombination in P3HT. This suggests that the quadrimolecular process is unique to regioregular polymers. As discussed in the next section, field-induced

ESR of P3HT has revealed the tendency of the formation of spinless doubly-charged state, the occurrence of quadrimolecular recombination may be reasonably understood.

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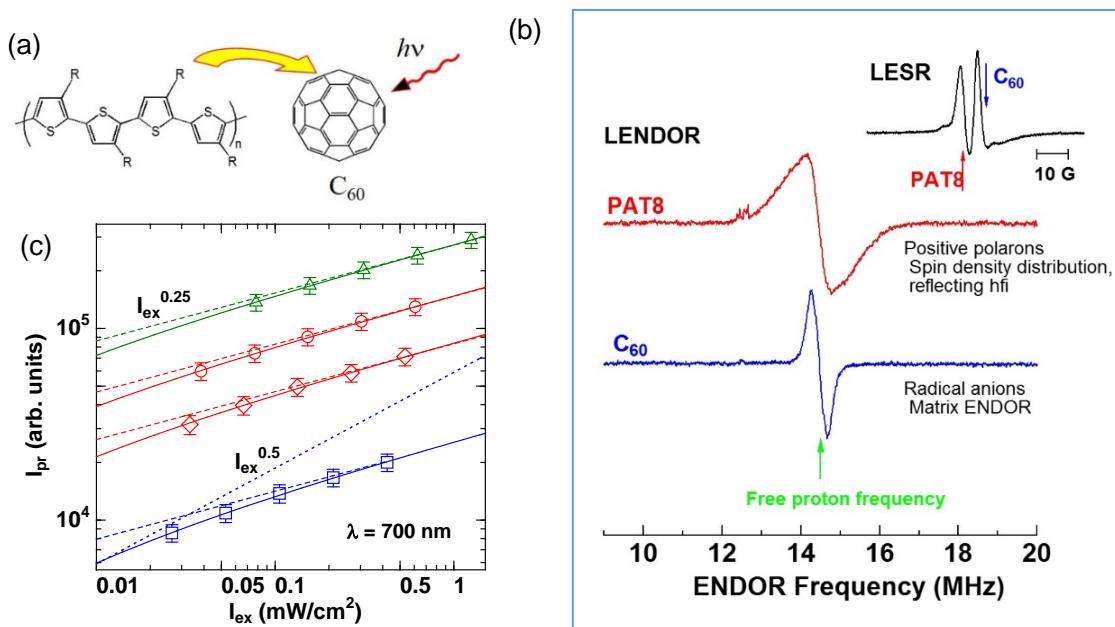


Fig. 3 (a) Molecular structure of P3AT/C₆₀ composite. (b) LENDOR signals of P3AT /C₆₀ composites. (c) Excitation power dependence of LESR signals.

4. Development of field-induced ESR spectroscopy – A new method for *in-situ* observation of charge carriers in organic transistors

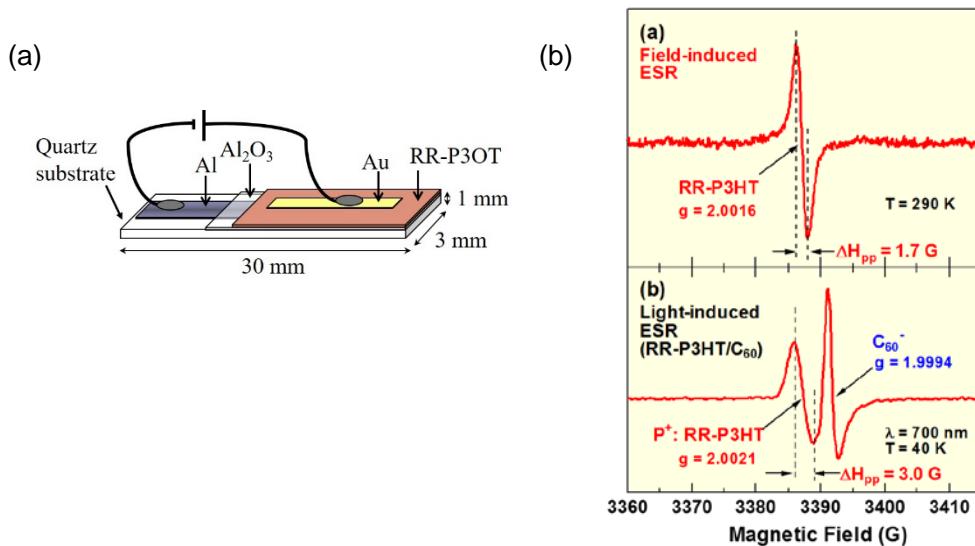
4-1. Initial development of field-induced ESR - Observation of polarons in field-effect devices of polyalkylthiophene

In organic field-effect devices such as organic transistors, charge carriers are accumulated at the semiconductor/insulator interface and exhibit transport. There have been preceding studies in detecting such interfacial carriers using various kinds of optical spectroscopic methods. On the other hand, however, there were no report of the detection of spins of interfacial carriers. By constructing field-effect devices suitable for ESR measurements using P3HT as a semiconductor, we have been successful in observing the first field-induced ESR (FI-ESR) signals of polarons injected at the semiconductor/insulator interface [1, 2].

The device structure of the first successful ESR measurements was a Metal-Insulator-Semiconductor (MIS) diode fabricated on a quartz glass substrate with vapor-deposited Al gate electrode, sputtered Al_2O_3 gate insulator and a drop cast film of the polymer with top Au electrode (Fig. 4(a)). Since P3HT is a p-type semiconducting material, upon applying negative gate bias, positive carriers are accumulated at the device interface and their ESR signals have been detected for the first time (Fig. 4(b)). The g -value of FI-ESR signals coincided well with those of positive polarons observed by light-induced ESR of P3HT/ C_{60} composites (Fig. 4(b)), providing evidence that the detected field-induced ESR signals originate from P3HT. In addition, when we rotate the device under the magnetic field, both the g -value and hyperfine-determined linewidth exhibited clear angular dependence, which directly shows the edge-on orientation of the polymer plane consistent with the formation lamellar crystalline structure at the device interface, as in Fig. 4(c).

Furthermore, the number of spins obtained from ESR signal and the number of charges calculated from the capacitance of the device coincided well, when the gate bias was low, showing that all the injected charge has spin, that is, polarons (Fig. 4(d)). By increasing the gate bias, however, spin number tends to show saturation, suggesting the formation of spinless bipolarons (or polaron pairs) as a carrier species. From those results, it has become clear that field-induced ESR signals provide the information concerning electronic and spin states and interfacial molecular orientation, which are crucial in determining the device performance.

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- 2) K. Marumoto, Y. Muramatsu, Y. Nagano, T. Iwata, S. Ukai, H. Ito, S. Kuroda, Y. Shimoji and S. Abe, *J. Phys. Soc. Jpn.* **74**, 3066-3076 (2005).



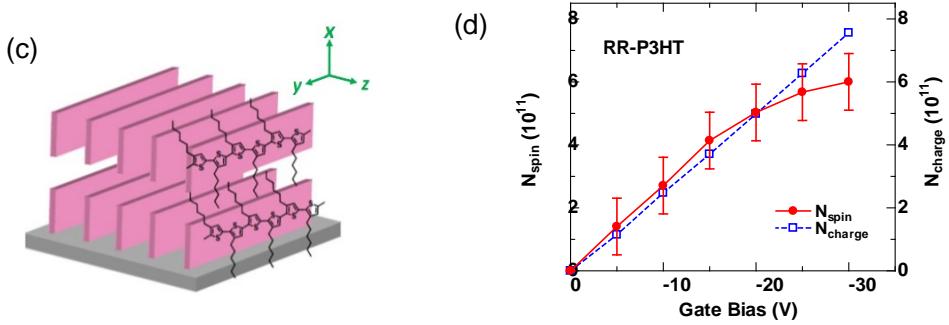


Fig. 4 (a) Schematic structure of a MIS diode for ESR measurements. (b) Comparison between the field-induced ESR signal of P3HT and light-induced ESR signal of P3HT/C₆₀ composite²⁾. (c) Molecular orientation of P3HT at the device interface. (d) Spin-charge relation of a MIS diode of P3HT²⁾.

4-2. ESR of pentacene transistors and spatial extent of wave function of polaron

FI-ESR started from MIS diode structure of P3HT. In the case of typical high-mobility small molecule, pentacene, we have fabricated field-effect transistor (FET) structure for FI-ESR and clear ESR signals have been successfully observed as in Fig. 5(a) [1]. The number of spin and the number of charge coincided well, showing the charges are polarons with spin. No spin saturation was observed in pentacene, contrary to the case of RR-P3HT, shown above. Angular dependence of *g*-value and hyperfine-determined ESR linewidth clearly showed the end-on type molecular orientation at the device interface (Fig. 5(b)).

Most striking result obtained from this study was the spatial extent of gate-induced positive polarons. Conventional picture of charge transport of pentacene was hopping transport of charge carriers localized on single molecule. From the analysis of hyperfine-determined ESR line width, spatial extent of polaron wave function was estimated to be about 10 molecules. This provided the first microscopic evidence for the band-like transport in the case of high-mobility small molecule.

FI-ESR method was adopted in other research groups, for example for pentacene transistors to study carrier dynamics. These results establish that the field-induced ESR is a new spectroscopic technique to probe the charge carriers at the interface of organic transistors by the detection of spin.

- 1) K. Marumoto, S. Kuroda, T. Takenobu and Y. Iwasa, *Phys. Rev. Lett.* **97**, 256603-1-256603-4 (2006).
- 2) H. Tanaka, M. Hirate, S. Watanabe, K. Kaneko, K. Marumoto, T. Takenobu, Y. Iwasa, and S. Kuroda, *Phys. Rev. B* **87**, 045309-1-4 (2013)

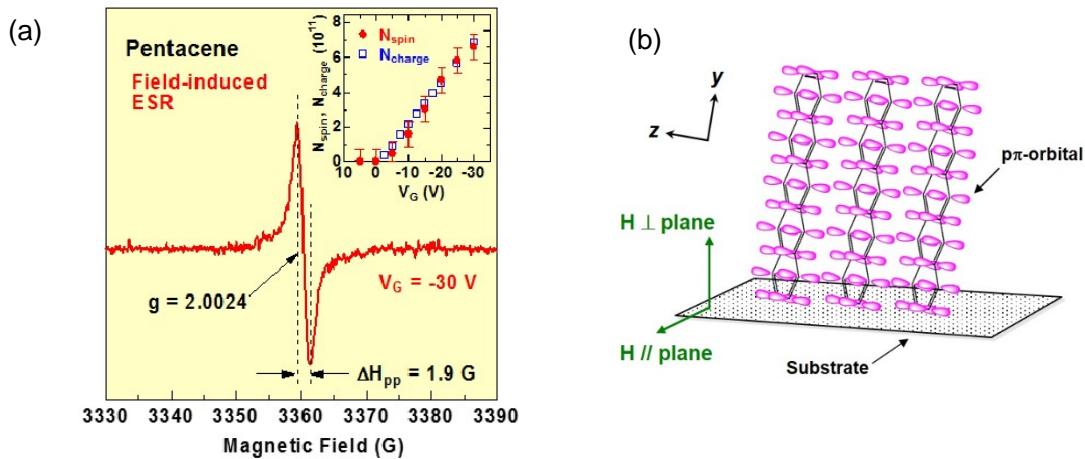


Fig.5 (a) FI-ESR signal of pentacene transistor and inset shows spin-charge relation^{1).} (b) Orientation of pentacene molecule at the device interface^{1).}

4-3. ESR of uniaxially aligned ultrathin polymeric transistors

Fabrication of polymeric transistors with uniaxially aligned polymer chain axis may attract interest both from the applications and basic studies of materials properties. As a fabrication method of such transistors, we have adopted Langmuir-Blodgett (LB) method that can fabricate ultrathin films by layer-by-layer depositions of a monolayer film formed on the water surface. By using newly developed LB technique employing co-spreading mixed solution of P3HT and a liquid-crystalline molecule on the water surface, and subsequent uniaxial compression orientation of monolayer film, uniaxially-aligned ultrathin monolayer transistors of P3HT were fabricated as shown in Fig. 6(a) [1]. For ESR measurements, we used low-doped $\text{SiO}_2/\text{n}^+/\text{Si}$ substrates that we have developed for FI-ESR, which do not deteriorate the Q-value of ESR sample cavity. Monolayer transistors showed good mobilities comparable to conventional P3HT transistors, providing evidence that the active layer thickness of charge transport is indeed single monolayer. The mobility along the chain direction was about two times larger than that of perpendicular direction. This weak anisotropy may be ascribed to the quasi two-dimensional charge transport resulting from the development of π - π stacking in a lamellar structure of P3HT.

Figure 6(b) shows the anisotropy of ESR signals in the two types of devices with different preferential chain orientations, the upper and lower curves with the chain direction perpendicular and parallel to the source-to-drain axis on the substrate, respectively. In particular, the g value along the chain direction (g_y) takes a minimum value, which was well reproduced from the DFT calculation. Using a spectrum simulation method, asymmetric ESR line shapes of the parallel and perpendicular chain orientations were well reproduced,

from which the in-plane orientation distribution function of the chain axis was quantitatively determined. The results well explained the observed dichroic ratio determined by polarized optical absorption measurements of P3HT ultrathin films. Thus by using of uniaxially aligned thin-film transistor structures, orthorhombic principal g-values of the P3HT chain were directly resolved for the first time, successfully showing the preferential in-plane orientation of the chain axes by a microscopic measurement.

- 1) S. Watanabe, H. Tanaka, S. Kuroda, A. Toda, S. Nagano, T. Seki et al., *Appl. Phys. Lett.* **96**, 173302-1-3 (2010).

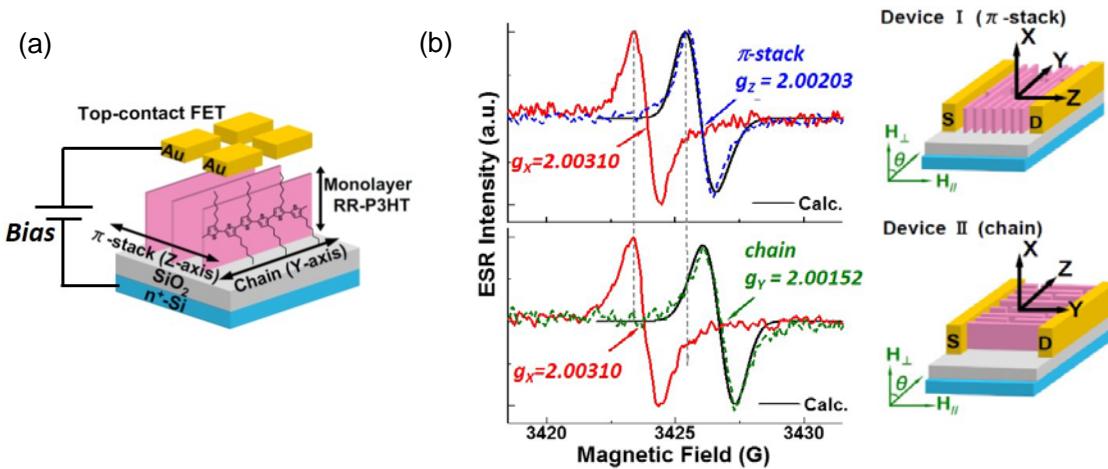


Fig. 6 (a) Schematic structure of monolayer organic transistor of P3HT¹⁾. (b) ESR signal anisotropy in two kinds of ultrathin FET devices of P3HT with in-plane preferential chain orientations¹⁾. The upper signals corresponds to the device structure with the chain orientation perpendicular to the channel direction (source and drain direction) and the lower ones to that with the chain parallel to the channel direction.

4-4. Low-temperature ESR of thienothiophene-based high-mobility small molecules

Thienothiophene-based molecules are typical high-mobility small molecules with high crystallinity, resulting from the strong intermolecular interaction through the sulfur atoms of thienothiophene base. C₁₀-DNTT is a typical thienothiophene-based high-mobility molecule of which field-effect transistors exhibit mobilities higher than 1cm²/Vs even in polycrystalline thin-film devices. Molecular structure of C₁₀-DNTT is shown in Fig. 7(a). To understand the transport mechanism of such high-mobility system, low-temperature carrier dynamics generally is an important issue, however, transport measurements become difficult at low temperatures due to the charge carrier trapping at grain boundaries. On the other hand, field-induced ESR can be measured regardless of grain boundaries [1], and ESR reveals the carrier motion even at 4K within the crystalline grains.

FI-ESR signals of C₁₀-DNTT thin-film transistors on SiO₂/n⁺-Si substrates were observed down to 4K [2]. FI-ESR spectra at 4K shows a clear angular dependence as in Fig. 7(b) where Θ denotes the angle between the external field and the normal direction of the substrate. ESR separates intra and intergrain motion from the motional effect of ESR signals depending on the magnetic field orientation. ESR at perpendicular direction ($\Theta = 0^\circ$) shown at the bottom of Fig. 7(b), all the crystalline grains make the same angle with the magnetic field, giving single ESR line (g_y) and yields the *intragrain* information. On the other hand, ESR at parallel direction ($\Theta = 90^\circ$) at the top of Fig. 7(b), randomly oriented grains gives two-dimensional powder ESR pattern (g_x and g_z) and yields *intergrain* information.

Anisotropy of principal g -values in Fig. 7 (b) were well reproduced by DFT calculation. Angular dependence of ESR signal was further reproduced well by spectrum simulation, from which the end-on molecular orientation (Fig. 7(a)) with very low angular fluctuation (<0.5°) has been revealed, showing that highly organized orientational order exists at the device interface. This may be one of the reasons for the high carrier mobility.

As for intragrain motion, sharp *Lorentzian* line shape characteristic of motional narrowing at $\Theta = 0^\circ$ signal gives direct evidence for the carrier motion within grain even at 4K. On the other hand, considerably low activation energy of intergrain motion was found from the temperature dependence of the ESR signal of parallel direction shown in Fig. 7(c). In the figure, typical motional narrowing phenomenon, that is, the static powder ESR spectra of two resolved peaks at 4K are drastically narrowed into a single resonance line at higher temperatures. From the analysis of the temperature dependent motional narrowing effect of the ESR signal, the activation energy of intergrain motion as low as 10 meV has been revealed. This value coincided well with the activation energy of about 10meV for FET mobility, of which temperature dependence is shown in the inset of Fig. 7(c). Such coincidence shows the microscopic origin of the activation energy of FET mobility governed by grain boundaries. This value may be one of the lowest values ever reported for the activation energy of FET mobility of organic transistors.

Finally, the spatial extent of the carrier wave function is of much interest in view of those highly mobile nature of charge carriers in C₁₀-DNTT. The observed ESR linewidth in the static limit indicates the extension ~100 molecules, much more delocalized in the case of pentacene of ~10 molecules. Such difference may be related to more flexible crystalline structure of pentacene, as discussed in the structural and Hall-effect measurements.

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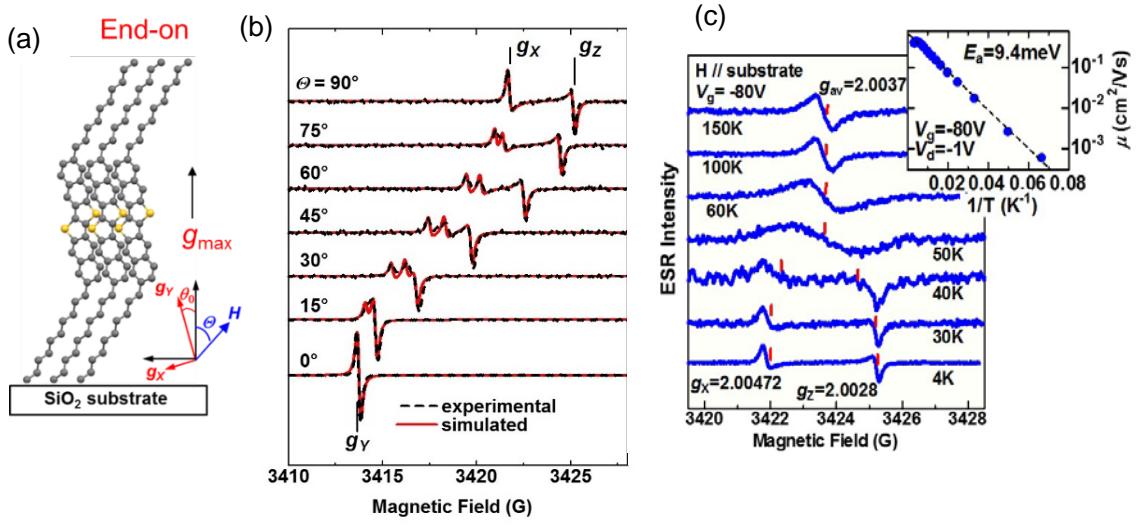


Fig. 7 (a) Molecular structure of C₁₀DNTT and the end-on molecular orientation at the device interface. (b) Angular dependence of ESR spectra of C₁₀DNTT (dotted line)²⁾. The angle Θ shows that between the external field and the normal direction of the substrate as shown in Fig. 7(a). Calculated ESR spectra are shown by solid line. (c) Temperature dependence of the ESR signals with the external field parallel to the substrate²⁾. Inset shows the temperature dependence of the field-effect mobility.

5. ESR of charge carriers in semicrystalline polymer PBT TT induced by chemical doping or ionic-liquid-gated transistor structures.

To date, many conducting polymers have been synthesized as new polymeric semiconducting materials aiming for the development of organic electronic devices. Recently, highly-doped state of semicrystalline conjugated polymers attract attention not only from the development of metallic conductivity, but also from thermoelectric applications. Concerning the metallic transition process, however, despite theoretical predictions about the change of electronic states of the carriers from polarons, via bipolarons to metallic state by doping (Fig. 8(a)), clear experimental evidence for such phenomena has not yet been well established. Since bipolaron is a doubly charged state without spin ($Q= \pm 2e$, $S=0$), we have been recently successful in showing that ESR is a suitable method to discriminate spinless bipolarons from polarons, by probing whether the charges induced by doping in semicrystalline polymers are ESR detectable or not.

In a semicrystalline conjugated polymer PBT TT, appearance of high conductivity in thin films by chemical doping using a fluoro-alkylsilane (FTS) molecules attracted considerable attention. We have carried out simultaneous measurements of conductivity and ESR using

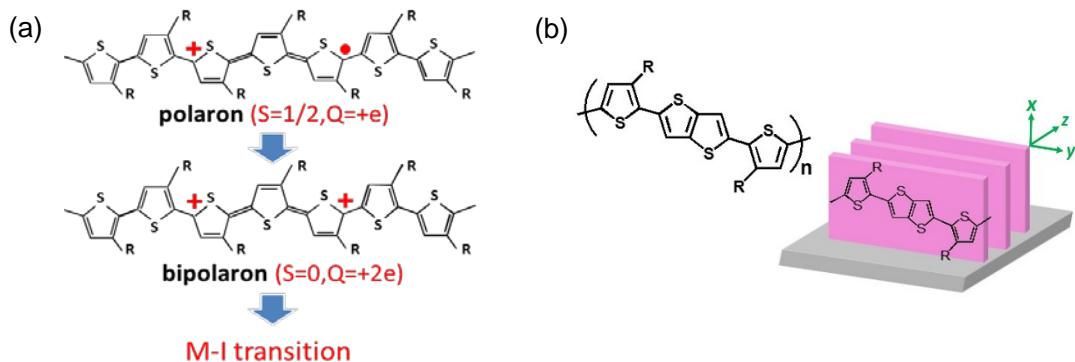
thin-film samples and successfully detected Pauli spin susceptibility characteristic of metals only in the crystalline domains with edge-on molecular orientations (Fig. 8(b)), providing microscopic evidence for the realization of metallic state in semicrystalline polymers [1].

More recently, we have succeeded in observing high conductivities and at the same time a metallic temperature dependence for certain temperature range by reversible electrochemical doping using ionic-liquid-gated transistor structures. Then we proceeded to construct ionic-liquid-gated transistor structures suitable for ESR measurements (Fig. 8(c)) and clearly observed ESR signals as in Fig. 8(e), showing the appearance of spinless bipolarons in high doping levels from the spin susceptibility [2]. By increasing the doping level, a clear decrease of spin numbers was observed while the charge numbers kept increasing as shown in Fig. 8(f). Bipolaron formation was also supported by the change of optical absorption upon electrochemical doping by ionic-liquid gating (Fig. 8(d)). In addition, angular dependence of ESR line width at high-doping regimes clarified the appearance of spin relaxation characteristic of conduction electrons (Elliott type). On the other hand, *g*-value anisotropy confirmed the edge-on molecular orientation was maintained up to the highest doping levels, showing the robust structure of the semicrystalline polymer.

Furthermore, by using bilayer films of F₄-TCNQ and PBTETT, a solid state diffusion of F₄-TCNQ into PBTETT films was found to take place, resulting in the appearance of Pauli susceptibility together with the observation of nearly ideal Hall effect at low temperatures, providing clear evidence for metallic transition in PBTETT films [3].

These results indicate that the control of electronic states from polarons via bipolarons to metallic state are becoming possible by reversible electrochemical doping process. Further studies of these electronic state transitions in other semicrystalline conjugated conducting polymers may contribute, for example, to deepen the understanding the electronic states of conjugated polymers and the development of their control methods.

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- 2) H. Tanaka, S. Nishio, H. Ito, and S. Kuroda, *Appl. Phys. Lett.* **107**, 243302 (2015).
- 3) K. Kang, S. Watanabe, H. Tanaka, S. Kuroda, H. Sirringhaus et al., *Nature Mater.* **15**, 896-902 (2016).



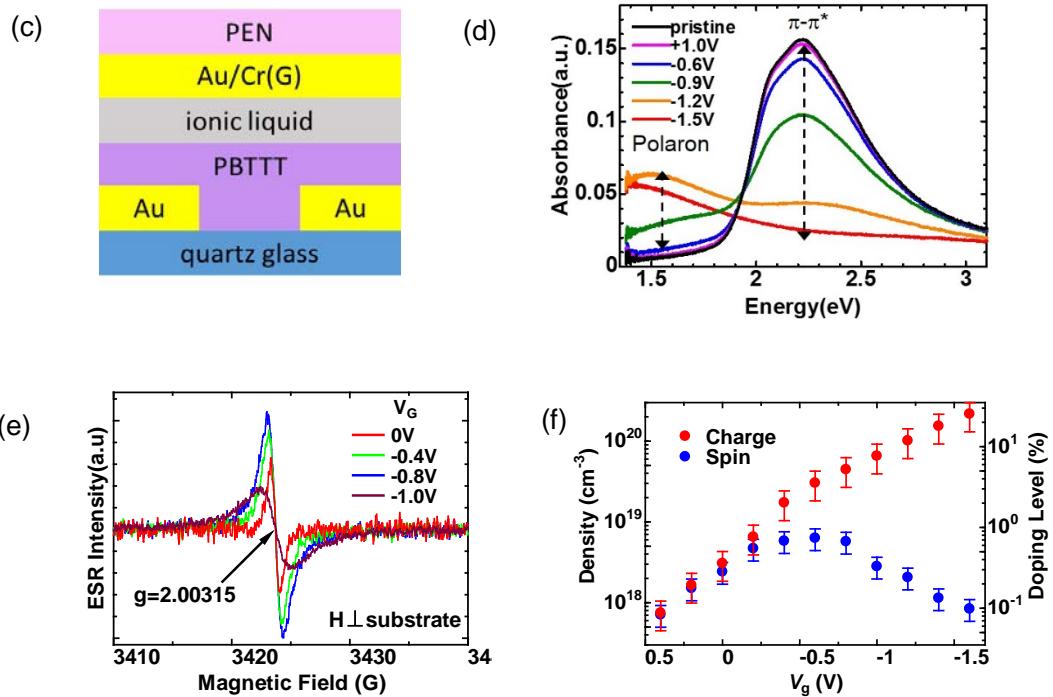


Fig. 8 (a) Polaron and bipolaron in P3HT. (b) Molecular structure of a semicrystalline polymer, PBTTT and edge-on molecular orientation at the device interface. (c) Schematic structure of an ionic-liquid-gated organic transistor. (d) Gate-bias dependence of optical absorption spectra of an ionic-liquid-gated MIS diode of PBTTT²⁾. (e) Gate-bias dependence of ESR signals in an ionic-liquid-gated transistor of PBTTT²⁾. (f) Spin-charge relation of ionic-liquid-gated transistors of PBTTT²⁾.

Publication List

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Original Papers

1. M. Date, M. Motokawa, H. Hori, S. Kuroda and K. Matsui
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