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Theoretical ESR *g* Values in Rubrene and Oligoacenes: Implication to Molecular Orientation at Interfaces in Organic FETs

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Using density functional theory calculations, molecular g tensors are theoretically investigated for rubrene and oligoacenes. The anisotropy in the calculated g shifts of rubrene well explains experimental results observed by field-induced electron spin resonance (FI-ESR) measurements. We demonstrate that the combination of the FI-ESR technique and the calculation of molecular g tensor is a quite useful approach to determine the molecular orientation at interfaces in organic field-effect transistors.

Keywords *g* tensor; rubrene, oligoacene; pentacene; density functional theory; electron spin resonance; organic field-effect transistor

Introduction

Organic field-effect transistors (OFETs) have been extensively investigated due to their potential advantages like flexibility, low-cost, and large-area [1,2]. Molecular orientation at interfaces in OFETs is considered as a key factor to control their electronic properties. This is because the intermolecular overlaps of directional π orbitals are responsible for transport whether it is bandlike or hopping type. Therefore, it is significant to determine and control the molecular orientation at the interfaces of OFETs for understanding the basic physics of the devices as well as their further performance improvement.

Recently, field-induced electron spin resonance (FI-ESR) technique has been successfully developed and applied to OFETs [3–7]. This measurement detects charge carriers with spins injected by a bias electrostatic field. These carriers are considered to be localized at interfaces between organic semiconductor and insulator in the devices, to which it is rather difficult to access using usual surface probe techniques. The FI-ESR measurement provides various insights for injected carriers such as the number of carriers, their spatial extent, and dynamics. It is also possible to determine molecular orientation at the interfaces in OFETs by analyzing the angular dependence of ESR spectra as a function of the direction

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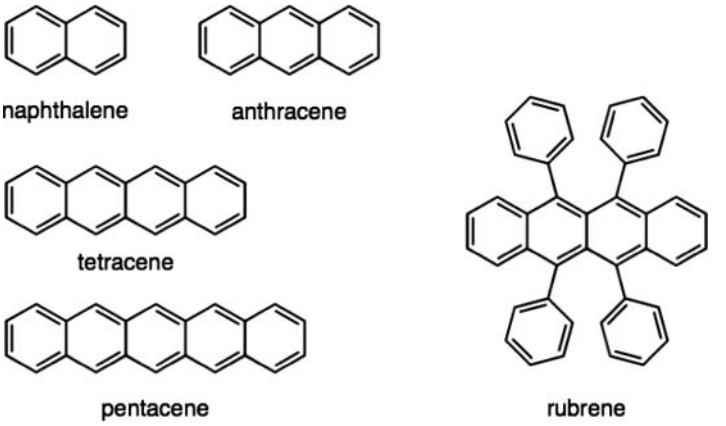

Scheme 1.

of external magnetic field. The anisotropy in g tensors or in hyperfine coupling tensors of constituting molecules is essential information for this analysis.

In the present report, we theoretically investigate the molecular g tensors of rubrene and oligoacenes using density functional theory (DFT) calculations. See Scheme 1 for the chemical structures of the molecules we investigate. We compare the theoretical results with the observed FI-ESR spectra of rubrene single crystals and discuss the molecular orientation at the FET interface.

Calculation

In molecule or condensed state, the g value deviates from that of a free electron, g_e (= 2.002 319 . . .), and is treated as a tensor: $g_{ij} = g_e\ \delta_{ij} + \Delta g_{ij}$, ($i,j = x, y,$ and z) where δ_{ij} is the Kronecker delta. The g shift, Δg_{ij}, comes from three contributions: a relativistic mass correction, a diamagnetic correction, and a contribution from a cross term between the orbital Zeeman and spin-orbit coupling operators. Anisotropy in g tensor arises from the latter two terms.

The DFT calculations were carried out for the cationic states of isolated molecules of rubrene and oligoacenes from naphthalene to pentacene (Scheme 1). The g tensors were calculated using the coupled-perturbed self-consistent field (CP-SCF) equation with the gauge-independent atomic orbitals. We mainly present the results obtained with the UB3LYP functional and 6–31G(d) basis set. We also examine the functional and basis set dependence. The molecular geometries were taken from the crystal structures [8–12]. The calculations were performed using the Gaussian 03 package [13].

Results and Discussion

Table 1 summarizes the principal values of the calculated g tensors of oligoacenes and rubrene. We take the X, Y, and Z principal axes so that they are close to the molecular short and long axes and the normal to the molecular plane, respectively.

The largest g shift is along the Y axis commonly in the molecules in Table 1. In naphthalene, the calculated g values agree well with the observed ones including their

Table 1. Principal g values, g_i ($i = X$, Y, and Z) of oligoacenes and rubrene calculated at the B3LYP/6-31G(d) level. Their g shifts, Δg_i, in the unit of ppm are also included.

		g_X	g_Y	g_Z	Δg_X	Δg_Y	Δg_Z
naphthalene		2.0024	2.0031	2.0027	107	757	350
anthracene		2.0025	2.0031	2.0026	220	768	242
tetracene	mol. A[a]	2.0026	2.0031	2.0025	290	759	184
	mol. B[a]	2.0026	2.0031	2.0025	296	764	188
pentacene	mol. A[a]	2.0027	2.0031	2.0025	333	742	143
	mol. B[a]	2.0027	2.0031	2.0025	332	737	137
rubrene[b]		2.0025	2.0030	2.0023	171	699	10

[a]mol. A and mol. B denote symmetrically inequivalent molecules in a unit cell.
[b]Reference [5].

ordering of magnitude: They were experimentally determined as $g_X = 2.0024$, $g_Y = 2.0028$, and $g_Z = 2.0025$, respectively, in our definition of the coordinate system [14]. When the molecule becomes longer from naphthalene to pentacene in oligoacenes, g_X increases while g_z decreases. The g shifts are nearly uniaxial with $g_X \sim g_Z$ in anthracene. In pentacene and rubrene, typical OFET materials, they are rather separated with each other with the ordering of $g_Y > g_X > g_Z$, indicating the orthorhombic nature of the g tensors. In tetracene and pentacene, two symmetrically inequivalent molecules in a unit cell (mol. A and mol. B in Table 1) [11] give almost the same g shifts.

Here, we examine the functional and basis-set dependences of the calculated g tensor of a rubrene cation molecule as an example. As seen in Table 2, the dependences are rather small, except for the Hartree-Fock method. Δg_X and Δg_Z, in particular, the former, decrease with increasing the weight of the Hartree-Fock exchange functional.

Next, we analyze the observed FI-ESR spectra of rubrene single crystals [5] using the calculated principal g values mentioned above. Solid circles in Fig. 1 indicate g values experimentally determined for carriers at the FET interface of rubrene single crystals. The value shows a characteristic dependence on the direction of the applied magnetic field $\boldsymbol{H}$.

Table 2. Functional and basis set dependences of the calculated g shifts of a rubrene cation molecule in the unit of ppm.

Functional	Basis set	Δg_X	Δg_Y	Δg_Z
UBLYP	6-31G(d)	187	678	22
UB3LYP	6-31G(d)[a]	171	699	10
	cc-pVDZ	165	712	8
	6-311G(d)	162	749	5
	cc-pVTZ	163	743	3
UBHandHLYP	6-31G(d)	128	721	–10
UHF	6-31G(d)	–2	718	–35

[a]Reference [5].

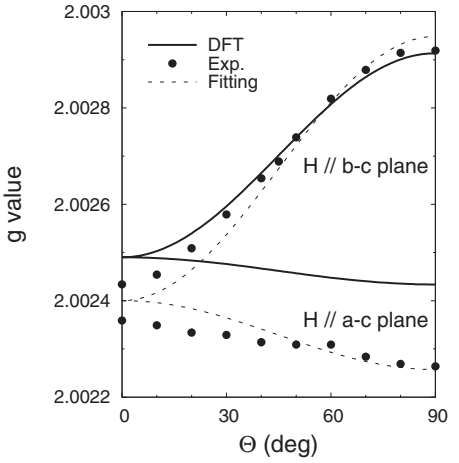

Figure 1. Angular dependence of ESR g values in rubrene single crystals. The external magnetic field $\boldsymbol{H}$ is inclined within the b-c and a-c planes of the crystal. Solid curves indicate theoretical ones obtained from the calculated principal g values. Solid circles are the FI-ESR experimental data for the carriers at the FET interface and dashed curves are their fitting curves [5].

We define Θ as the angle between $\boldsymbol{H}$ and the c axis of the crystal. When $\boldsymbol{H}$ is inclined within the a-c and b-c planes, the g value is supposed to vary as

$$g(\Theta) = g_e + \Delta g_X \cos^2\Theta + \Delta g_Y \sin^2\phi \sin^2\Theta + \Delta g_Z \cos^2\phi \sin^2\Theta \quad (a\text{-}c \text{ plane}),$$
$$g(\Theta) = g_e + \Delta g_X \cos^2\Theta + \Delta g_Y \cos^2\phi \sin^2\Theta + \Delta g_Z \sin^2\phi \sin^2\Theta \quad (b\text{-}c \text{ plane}),$$

respectively, if the g shift is not large as in the present case. Here, ϕ is the angle between the principal Y axis and the b axis and is calculated as 22.96 deg in the DFT method. The solid curves in Fig. 1 indicate the g values calculated using the above equations with the principal g shifts listed in Table 1. Their angular dependence strongly reflects the orthorhombic nature of the g shifts. The theoretical curves reproduce well the features of experimental results. In this analysis, we assume molecular orientation in bulk crystal [8]. Therefore, we can conclude that the molecular orientation is essentially same at the FET interface and in the bulk for rubrene single crystals.

Summary

In this report, we have theoretically investigated the molecular g tensors of rubrene and oligoacenes using DFT calculations. Rubrene and pentacene, typical OFET materials, have g shifts of the orthorhombic nature. The angular dependence of the g values observed by the FI-ESR experiment for rubrene single crystals is well explained by the g shifts calculated by the DFT method with assuming the same molecular orientation between the FET interfaces and bulk crystal. This work demonstrates that the combination of the FI-ESR technique and the calculation of molecular g tensor is a quite useful approach to determine the molecular orientation at interfaces in OFETs.

Acknowledgments

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