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Electron Spin Resonance of Thin Films of *N*,*N*′-Di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (NPB) Doped by Iodine Vapor

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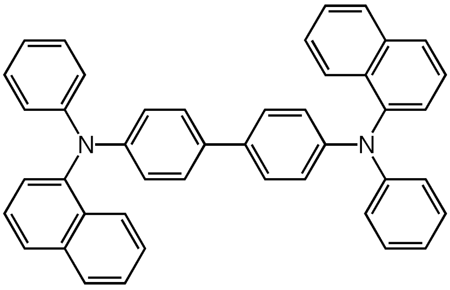
We have successfully observed the ESR signals of radical cations in the thin films of *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (NPB), typical hole-transport material, for the first time to our best knowledge. In order to characterize the radical cation state, ESR spectra obtained upon chemical doping with iodine are analyzed combined with density functional theory (DFT) calculation. The ESR line width is inversely correlated with doping concentration.

Organic light-emitting diodes (OLEDs) have been actively studied because of their excellent characteristics such as high efficiency, low cost productivity, and flexibility.[1,2] Aromatic amines are widely used as hole-transport materials in the devices. Among them, *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (NPB) (Scheme 1) is a typical one with high thermal stability.[3] Blue-color luminescence was also reported in an OLED containing NPB layer.[4] In order to understand the hole-transport properties, it is quite important to elucidate the nature of cationic state. Since cations are usually accompanied by radical spins, electron spin resonance (ESR) spectroscopy is a useful technique for this purpose. Although the thin films of NPB have been characterized by various methods like photoemission,[5] time-of-flight,[6] infrared,[7] and Raman spectroscopies,[8] the ESR study of NPB film has not been reported to our best knowledge. We have utilized this technique for other organic materials in thin films[9] and in organic devices.[10–12] In the present letter, we carried out chemical doping by exposing the NPB films to iodine vapor and successfully observed ESR signals arising from the induced radical cations. We also performed density functional theory (DFT) calculations to obtain insights to the radical cation state.

By thermal vacuum evaporation under the pressure of 4×10^{-4} Pa, NPB was deposited on a quartz substrate cleaned with isopropyl alcohol and acetone. The NPB film is 80 nm in thickness and 0.84 cm^2 in area. Subsequently, the film was doped using iodine vapor under vacuum of 1×10^{-1} Pa for 1 h, then it was sealed in an ESR sample tube. The doping concentration was reduced by exhausting the sample tube using a diffusion pump and was controlled by the length of the exhaustion time. ESR measurements for the sample were performed with a JEOL JES-FA200 ESR spectrometer.[13] DFT calculations of the B3LYP/6-31G(d) level were carried out for an isolated NPB cation.[14] The molecular geometry was fully optimized. The principal values of g tensor were computed using the gauge-independent atomic orbital method.



Scheme 1. Chemical structural formula of NPB.

Figure 1 shows observed ESR spectra: (a) spectrum observed right after the iodine doping and (b) that measured after an exhausting time of five hours. As seen in this figure, clear ESR signals were observed in both cases. In Figure 1a, g value, peak-to-peak ESR line width ΔH_{pp}, and spin concentration of the ESR spectrum are 2.0040, 0.676 mT, and 2.65×10^{20} cm^{-3}, respectively. Meanwhile, in Figure 1b, they are 2.0036, 1.06 mT, and 2.12×10^{19} cm^{-3}, respectively. The spin concentrations were estimated by assuming that the NPB films are doped homogeneously over their volumes and correspond to a doping level of 50% per volume molecules in Figure 1a and 4% in Figure 1b. Here, the doping level per volume molecules means the number of spins per one molecule estimated under the aforementioned assumption.

Here, we examine the g values mentioned above. They are similar in both spectra in Figure 1. The three principal values of

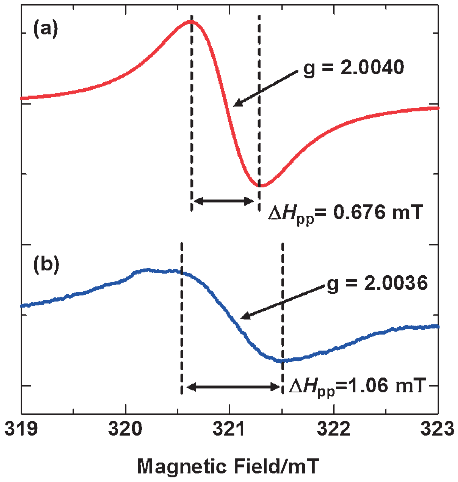


Figure 1. ESR spectra of thin iodine-doped NPB film. (a) Spectrum observed right after the iodine doping and (b) that measured after an exhausting time of five hours.

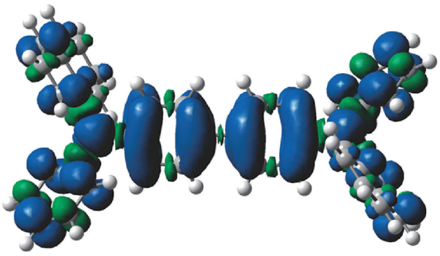


Figure 2. Spin density profile of a NPB cation calculated at the B3LYP/6-31G(d) level.

g tensor were calculated as 2.0025, 2.0028, and 2.0034, which are consistent with the experimental values. A close g value of 2.004 was reported for *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMB).[15] We also measured the ESR spectra by changing the direction of the external magnetic field, but the spectra did not show any anisotropy in g value, consistent with the amorphous nature of the sample. Here, we comment on a previous study for a hole-only device of ITO/Alq_3/NPB/Ag with electrically detected magnetic resonance (EDMR).[16] Although the authors did not mention explicitly the origin of the EDMR signal, the g value of the EDMR signal was reported to be 2.0031, which is close to those of our experimental and theoretical results.

Next, we discuss the ESR line width. The origin of the rather broad line width in Figure 1b is thought to arise from hyperfine interactions between electron spins and nuclei of hydrogen and nitrogen atoms. Figure 2 shows the spin density profile calculated by DFT. According to the natural population analysis, the nitrogen atoms have the largest weight of spin density and are considered to be a major contribution to the hyperfine coupling. The observed line width of 1.06 mT is narrower than that in TMB (2.8 or 2.3 mT),[15,17] which is probably due to the lack of methyl groups in NPB.[17] Other possible reasons are the extension of a spin over multiple molecules in the thin film[10] and the motional narrowing described below.

As seen in Figure 1, ΔH_{pp} becomes narrower when spin concentration increases. This correlation was examined in more detail by changing exhausting time and is clearly confirmed as seen in Figure 3. Moreover, the temperature dependence of ΔH_{pp} at a doping level of 15% per volume molecules (Figure 4) shows that ΔH_{pp} becomes broader when temperature is decreased. This temperature dependence clearly indicates the motional narrowing in which charge carriers feel an averaged magnetic field due to their hopping in amorphous solid. The concentration dependence of ΔH_{pp} can be explained as follows: The charge carriers are supposed to be confined in trap levels or to be confined by pinning potential due to the counter anions. When doping concentration increases, charge carriers reside at shallower traps or the pinning potential becomes averaged and varies more slowly in space, resulting in the carrier becoming more mobile and ΔH_{pp} becoming narrower. In the case of motional narrowing, ΔH_{pp} with broad Lorentzian line width is approximately proportional to trapping time of charge carriers τ_{tr}, which is considered to be governed by thermal activation.[12] The inset of Figure 4 shows the Arrhenius plot of ΔH_{pp}, and data above 200 K follows the activation formula [$\exp(\Delta/kT)$] with the activation energy Δ of 0.011 eV (the solid line in the inset). Further investigation will clarify the dynamical nature of charge carriers induced in NPB film.

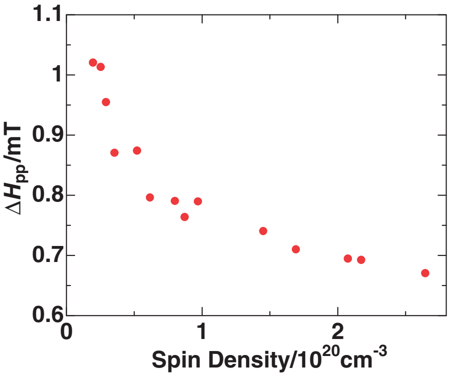


Figure 3. Correlation between ΔH_{pp} and spin concentration of thin NPB film.

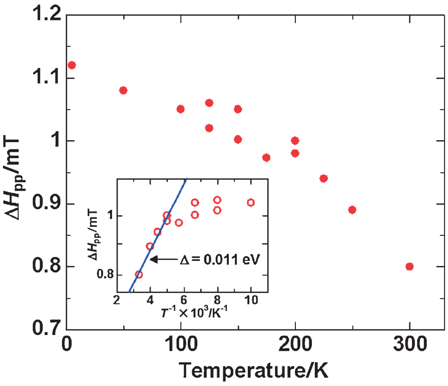


Figure 4. Temperature dependence of ΔH_{pp} of thin iodine-doped NPB film. Inset: Arrhenius plot of ΔH_{pp}. For 120, 150, and 200 K, we performed two independent measurements.

In conclusion, we have successfully observed ESR signals of thin NPB film for the first time. ESR measurement can assign molecular species using g values as their fingerprints. Therefore, this work offers a basis to characterize the charge carriers in NPB-based multilayered OLEDs and would open a way to understand issues in devices such as the mechanism of device degradation.

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