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3 **Direct observation of spins at bathocuproine (BCP)**
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6 **interfaces: an electron spin resonance study on BCP/metal (Al**
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9 **or Au) thin films**
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ABSTRACT

We report an electron spin resonance (ESR) study of the layered thin films of bathocuproine (BCP) and metal (Al or Au). Clear ESR signals with $g = 2.0030$ were observed for the samples containing Al owing to gap states at BCP/Al interfaces, while no ESR signal was observed for the samples containing Au. The ESR analysis shows that the spins are magnetically isolated with a maximum spin concentration of 1.7% per BCP monomer. The activation energy of spin motion is found to be very low, approximately 1 K, supporting the enhanced electrical conductivity in BCP layers with gap states.

Keywords: Bathocuproine (BCP), Electron spin resonance (ESR), Thin films, Organic/metal interfaces, Gap states, Activation energy

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1. Introduction

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]. They have improved their device performance drastically, and are now ready to be commercialized [3,4]. However, several problems still remain to be clarified such as interface phenomena in organic semiconductor devices [5-7]. Especially, controlling the electrical properties at the interfaces between organic semiconductors and metal electrodes is a key issue toward improving the carrier injection and thus their device performance [8-12].

For controlling the electrical properties at the organic/metal interfaces, electron buffer layers have often been introduced in OLEDs and organic photovoltaic cells (OPVCs). An electron transport compound bathocuproine (BCP) is one of the materials used most commonly as electron buffer [13-18]. Its chemical structure is illustrated in Figure 1a. It is reported that BCP has an energy difference of 3.5-3.7 eV between the highest occupied molecular orbital (HOMO) of 6.1-6.5 eV and the lowest unoccupied molecular orbital (LUMO) of 2.4-3.0 eV [19-21]. Insertion of the BCP layer between *n*-type semiconductor C₆₀ and cathode metals can greatly improve the power conversion efficiency of OPVCs [15,17]. Experimental and theoretical studies on the interactions

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3 between BCP and cathode metals have been reported [7,21-23]. **Studies of** ultraviolet
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6 photoelectron spectroscopy (UPS) have demonstrated the formations of gap states
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9 between the HOMO and LUMO levels at the interfaces [7,21,23]. **Formations** of the gap
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12 states sensitively depend on the work function of metals; the gap states are formed at the
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15 interfaces with metals that have lower work **functions** below 4.3 eV [7,21-23].
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19 Although the UPS studies have shown the existence of the gap states, these
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22 studies cannot directly clarify the spin states of the gap states and their concentration at
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25 the interfaces. It is important to further clarify the gap states from microscopic
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28 viewpoints, because it would provide useful insights towards improving the carrier
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31 injection at the organic/metal interfaces. However, **no** microscopic characterization of
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34 the gaps states **has yet** been performed.
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38 **Electron** spin resonance (ESR) spectroscopy is suitable for such microscopic
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41 characterization, because it can investigate organic semiconductors and their devices at
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44 the molecular level. Actually, we have clarified spin states of charge carriers and their
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47 spin concentration not only in organic semiconducting materials [24] but also in organic
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50 semiconductor devices such as organic field-effect transistors (OFETs) [25-27] and
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53 OPVCs [28,29]. Our ESR investigations **are also involved in the** charge-carrier states of
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56 radical cations in a typical hole-transporting material
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3 *N,N*-di(1-naphthyl)-*N,N*-diphenylbenzidine (NPB) [30] and radical anions in a typical
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6 organic light-emitting material tris(8-hydroxyquinoline) aluminum (Alq₃) [31,32]. We
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9 note that there is yet no ESR study of BCP on this issue.
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13 In the present paper, we report on the ESR study of the gap states formed at the
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16 BCP/metal interfaces to investigate the interactions between BCP and metals. We have
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19 observed ESR signals due to the gaps states that are formed at the interfaces between
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22 BCP and aluminum (Al). The obtained *g* value of the ESR signal is relatively close to
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25 the theoretical one for a radical anion calculated by density functional theory (DFT)
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28 method. Our findings demonstrate that the charge transfer occurs between BCP and Al
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31 at the interfaces, whereas no ESR signal has been observed when the metal is replaced
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34 to Au. This is consistent with the absence of the gap states at the BCP/Au interfaces.
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41 2. Experimental

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44 The structure of layered thin-film samples of BCP/metal and metal/BCP are
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47 shown in Figure 1b. In these samples, thin films of BCP with a thickness of 100 nm and
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50 metals (Al, Au) with a thickness of 50 nm were vapor-deposited on quartz substrates (3
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53 mm × 30 mm) cleaned with isopropyl alcohol and acetone. In the deposition, the
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56 vacuum chamber was kept at 2×10⁻⁴ Pa. The deposition rate for each BCP and metal is
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0.1 Å/s below 3 nm, 0.3 Å/s from 3 to 5 nm, and 1.0 Å/s above 5 nm. For comparison, BCP thin film with a thickness of 100 nm was also fabricated on a quartz substrate. The area of the layered thin films was 0.78 cm². Each sample was put in an ESR sample tube, which was evacuated to 2×10⁻⁵ Pa, and then finally sealed under vacuum conditions or in a He gas atmosphere at 1.33×10⁴ Pa.

ESR measurements were performed in the range of 5 and 300 K using a JEOL JES-FA200 X-band spectrometer with a JEOL ESCT470 cryostat. The absolute magnitudes of the *g* value, the ESR linewidth, and the number of spins were calibrated using a standard Mn²⁺ marker sample. The spin susceptibility and the number of spins of the samples were obtained by integrating the ESR signal twice and by comparison with that of the standard marker in which the number of spins was known.

DFT calculations of an isolated BCP anion were also performed in order to discuss the observed *g* value. The calculation was done with the UB3LYP functional and the 6-31G(d) basis set using the Gaussian 09 package [33]. The geometry was fully optimized for its anionic state.

3. Results and discussion

3.1. ESR signals of the interfaces between BCP and metal

First, we show the ESR signals of the three kinds of samples: BCP/metal, BCP thin film, and metal/BCP. Figures 2a and 2b show the ESR signals measured at 298 and 5 K, respectively. We have observed a clear ESR signal with $g = 2.0030 \pm 0.0001$ for the samples of BCP/Al and Al/BCP. This observation directly demonstrates the charge transfer between BCP and Al. This is because the BCP thin film without the metal shows no ESR signal as shown in Figure 2a. Note also that the possibility for the ESR observation of Al is excluded because its g value is known to be as 1.997 ± 0.001 [34], which is completely different from the observed value of 2.0030.

The UPS study has reported the electron transfer from metal to BCP [7]. Thus, the ESR observation microscopically demonstrates the electron transfer by detecting the spin formation. The observed electron transfer suggests the formation of the gap states at the interfaces between BCP and Al, where the work function (Φ_m) of Al is 4.2 eV [21]. However, no ESR signal was observed for the samples of BCP/Au and Au/BCP, which means the absence of charge transfer between BCP and Au. This finding is consistent with formation of no gap states at the interfaces between BCP and Au, where Φ_m of Au is 5.2 eV [7, 21].

Figures 3a and 3b show schematic energy diagrams of the Al/BCP (a) and Au/BCP (b) interfaces, respectively. Here, E_F , E_{VL} , and Δ_{VL} are the Fermi level, the

vacuum level, and the vacuum level shift, respectively. In (a), a schematic profile of the gap states is also shown. These diagrams are based on Refs. [7,21]. At the Al/BCP interface, the Fermi level of Al almost coincides with the LUMO level of BCP and the gap states are formed. Meanwhile, at the Au/BCP interface, the Fermi level of Au does not coincide with the LUMO level of BCP and the gap states are not formed.

Table 1 summarizes the observed g values and the full width at half maximum of the ESR linewidth $\Delta H_{1/2}$. The Φ_m values were taken from Refs. [7,21]. For the BCP/Al sample, the $\Delta H_{1/2}$ value was obtained by integrating the ESR signal as $\Delta H_{1/2} = 1.47 \pm 0.01$ mT at 298 K and 1.62 ± 0.01 mT at 5 K. For the Al/BCP sample, the value was 1.63 ± 0.01 mT at 5K. The observed ESR lineshape is a Lorentzian type, which can be explained by the motion of observed electron spins, as discussed in 3.4. Note that no clear anisotropy of the ESR signals for the samples of BCP/Al and Al/BCP was observed in the direction of the external magnetic field relative to the substrate, which confirms the amorphous nature of the BCP layers.

3.2. DFT calculation of BCP anionic state

Next, we show the results of the DFT calculation. Since the possibility of the formation of BCP radical cations is excluded because of the electron transfer from metal

to BCP as mentioned in 3.1 [7], we concentrate on anionic state in calculation. Figure 4 shows the spin-density profile of a radical anion on a BCP molecule. The three principal values of the g tensor were calculated as 2.0032, 2.0027, and 2.0014 for a BCP radical anion. The average of these calculated values, 2.0024, is relatively close to the experimental values (2.0030) presented in 3.1. The isolated anion is a crude model to compare with the experimental results. For calculating the g values in more realistic situation, we have to take care of interaction between a BCP molecule and metal [7,21,35]; previous DFT calculations pointed out the mixing of the wave functions of a BCP molecule and Al atoms [22] and the near-edge X-ray absorption fine structure (NEXAFS) measurements reported bond formation between metal and N in BCP [36].

We also comment that the relatively close g values between the experiment and calculation indicate an additional possibility that BCP radical anions are formed without contacting Al by electron hopping in BCP molecules because the Schottky barriers between Al and BCP are reduced by the formation of the gap states. This possibility is consistent with the absence of the clear anisotropy in the observed ESR signal. At present, we have confirmed the formation of the gap states and the electron transfer to BCP molecules for the interfaces between BCP and Al from the ESR observation, although further investigation is needed for clarifying that the observed spins are

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3 originated from whether BCP radical anions interacted with Al or isolated BCP radical
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6 anions formed by the electron hopping or both of them.
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16 To investigate the magnetic interaction among the spins at the interfaces
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18 between BCP and Al, we have measured the temperature dependence of the ESR signal
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20 of the samples of BCP/Al and Al/BCP. Figure 5 and its inset show the temperature
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22 dependence of spin susceptibility χ and inverse spin susceptibility $1/\chi$ of the samples of
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24 BCP/Al and Al/BCP. The inset clearly shows that χ obeys the Curie law. Thus, the spins
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26 at the interfaces between BCP and Al are magnetically isolated in the samples of
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28 BCP/Al and Al/BCP. This indicates that the observed Lorentzian ESR lineshape dose
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30 not originate from the exchange interaction among the observed spins. As discussed in
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46 The χ value of the BCP/Al sample is larger than that of the Al/BCP sample. The
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48 reason for this enhancement is attributable to the increase in the area of the interfaces
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50 between BCP and Al, because Al is supposed to penetrate into the BCP layer during the
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52 deposition of the Al layer on the BCP layer in this sample. Meanwhile, it seems hard
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that Al penetrate into the BCP layer in the Al/BCP sample. We will discuss the spin concentration at the interfaces between BCP and Al in 3.5.

3.4. Spin dynamics at the interfaces between BCP and Al

In this subsection, we discuss the spin dynamics at the interfaces between BCP and Al. Figure 6 shows the temperature dependence of $\Delta H_{1/2}$ of the samples of BCP/Al and Al/BCP. As clearly shown in Figure 6, $\Delta H_{1/2}$ monotonically decreases as temperature increases from 5 K up to ~ 50 K; then $\Delta H_{1/2}$ is almost temperature-independent up to 298 K.

This trend demonstrates the motional narrowing of the ESR linewidth due to the motion of spins by thermal activation energy as explained below. The static linewidth of the ESR signals of the samples of BCP/Al and Al/BCP is governed by hyperfine interactions between electron spins and nuclear spins of nitrogen and hydrogen in a BCP molecule (see Figures 1a and 4). If electron spins are immobile, the observed ESR linewidth does not depend on temperature because the hyperfine interactions does not alter [31,32]. However, if electron spins are thermally activated and become mobile in amorphous solids, the hyperfine interactions become averaged and effectively small, which results in the narrowing of the ESR linewidth [30]. From

the observation of the motional narrowing of the ESR linewidth, we conclude that a majority of the spins at the interfaces between BCP and Al are mobile. Note that the motional narrowing is consistent with the observation of the Lorentzian ESR lineshape shown in Figure 2.

The thermal activation energy of the spin motion can be evaluated from the Arrhenius plot of $\Delta H_{1/2}$. The inset of Figure 6 shows the results for the samples of BCP/Al and Al/BCP. Here, we explain the relation between the thermal activation energy and the ESR linewidth $\Delta H_{1/2}$. In the case of the motional narrowing of ESR linewidth with a broad Lorentzian lineshape, $\Delta H_{1/2}$ can be expressed using the trapping time (τ_{tr}) of electron spins as follows [26]:

$$\Delta H_{1/2} = 2 \gamma (\Delta H_d)^2 \tau_{tr} . \quad (1)$$

Here, γ is the gyromagnetic ratio for the BCP π electrons. ΔH_d is the static linewidth that arises from the hyperfine interactions with the nuclear spins. The probability of thermal detrapping of an electron spin from a trap state, $1/\tau_{tr}$, can be described by the following Arrhenius equation:

$$1/\tau_{tr} = A e^{-\Delta/kT} , \quad (2)$$

with the thermal activation energy Δ of the spin motion, in other word, the activation energy of charge carriers. Here, k , T , and A are the Boltzmann constant, temperature,

and a constant, respectively. By combining Eqs. (1) and (2), Δ can be determined from the temperature dependence of $\Delta H_{1/2}$. The Arrhenius plot of $\Delta H_{1/2}$ shown in the inset of Figure 6 evaluates Δ to be approximately 1 K for both samples of BCP/Al and Al/BCP. Δ gives the approximation of the trapping energy of charge carries. Therefore, this extremely low value of Δ supports the enhanced electrical conductivity in the BCP layer with gap states from microscopic viewpoints [7,37].

3.5. Spin concentration at the interfaces between BCP and Al

Finally, we discuss the spin concentration at the interfaces between BCP and Al. We estimate the number of spins for the Al/BCP sample. This is because the penetration of Al atoms in the BCP/Al sample hampers clear identification of the interface between the BCP and Al layers. From the ESR signal at 5 K, the surface concentration of the electron spins is evaluated to be $2.9 \times 10^{12} \text{ cm}^{-2}$ for the Al/BCP sample. If we tentatively evaluate the spin concentration for one BCP monolayer at the Al/BCP interface using the lattice constants of BCP crystals [38], this value gives a maximum spin concentration of 1.7% per BCP monomer, in other words, one spin per 58 monomers at the interface. The actual spin concentration is possibly lower than this value because the spin distribution for a few monolayers may exist along the normal to the BCP layer, as

suggested in 3.2. The spin formation with a relatively high concentration probably causes the Ohmic contact at the BCP/electrode interfaces, as discussed in Refs. [7,23,37]. However, this spin concentration is not too high for the spins to interact with each other, as confirmed by the Curie behavior as shown in Figure 5.

The surface concentration of the electron spins in the BCP/Al sample is nominally estimated to be $2.3 \times 10^{13} \text{ cm}^{-2}$ by the application of the same method. This value is larger than that of the Al/BCP sample and is reasonably explained by the penetration of Al into the BCP layer, as discussed in 3.3.

4. Summary

We have performed an ESR study of layered thin films of BCP and metal (Al or Au) and observed clear ESR signals of the samples of BCP/Al and Al/BCP, which are ascribable to the gap states at the interfaces between BCP and Al. The obtained g value of the ESR signal is relatively close to the theoretical value calculated by the DFT method for a radical anion on a BCP monomer. However, no ESR signal has been observed for the samples of BCP/Au and Au/BCP, which is consistent with the absence of the gap states at the interfaces between BCP and Au.

As for the BCP/Al and Al/BCP samples, the spin susceptibility obeys the Curie

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3 law, and the ESR linewidth $\Delta H_{1/2}$ shows motional narrowing. Thus, the electron spins at
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6 the interfaces between BCP and Al are shown to be isolated and mobile. The activation
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9 energy of the spin motion is evaluated to be ~ 1 K from the temperature dependence of
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12 $\Delta H_{1/2}$. The maximum spin concentration at the Al/BCP interface is quantitatively
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15 evaluated to be 1.7% per one BCP monomer. Therefore, the low activation energy and
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18 the relatively high concentration of spins accompanying gap states reasonably explain
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21 the enhanced electrical conductivity in the BCP layer with gap states; this enhancement
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24 is useful for improving the device performance by using BCP electron buffer layers in
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Table 1. Work function of metal Φ_m , g value, full width at half maximum of the ESR linewidth $\Delta H_{1/2}$.

sample	Φ_m (eV)	g value	$\Delta H_{1/2}$ (mT)	
			5 K	298 K
BCP/Al	4.2	2.0030±0.0001	1.62±0.01	1.47±0.01
Al/BCP		2.0030±0.0001	1.63±0.01	-
BCP/Au	5.2	not observed		
Au/BCP				
BCP	-	not observed

Figure 1. (a) Chemical structural formula of bathocuproine. (b) Cross section of the sample structures of layered thin films of quartz/BCP/metal (left figure) and quartz/metal/BCP (right figure), where the metal is Al or Au.

Figure 2. (a) ESR signals of the samples of BCP/Al (red solid line), BCP/Au (blue dashed line), and BCP thin film (black dotted line) at 298 K. (b) ESR signals of the samples of BCP/Al (red solid line) and Al/BCP (blue dashed line) at 5 K.

Figure 3. Schematic energy diagrams of (a) the Al/BCP interface and (b) the Au/BCP interface with energy levels of HOMO and LUMO of BCP. Here, E_F , E_{VL} , Φ_m , and Δ_{VL} are Fermi level, vacuum level, work function of the metal, and vacuum level shift, respectively. In (a), a schematic profile of the gap states is also shown. These diagrams are based on Refs. [7,21]

Figure 4. Spin density profile of a radical anion of a BCP molecule calculated by DFT method.

Figure 5. Temperature dependence of spin susceptibility χ of the samples of BCP/Al (solid circles) and Al/BCP (solid squares). Inset: temperature dependence of inverse spin susceptibility $1/\chi$ of the samples of BCP/Al (open circles) and Al/BCP (open squares).

Figure 6. Temperature dependence of $\Delta H_{1/2}$ of the samples of BCP/Al (solid circles) and Al/BCP (solid squares). Inset: the Arrhenius plot of $\Delta H_{1/2}$ of the samples of BCP/Al (open circles) and Al/BCP (open squares). Solid lines show least-squares fits to the data.