



Photoelectron Spectroscopy of Molecular Anion of Alq₃: An Estimation of Reorganization Energy for Electron Transport in the **Bulk**

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Supporting Information

ABSTRACT: A molecular anion of tris(8-hydroxyquinolinato)aluminum (Alq₃) was generated by a pulsed discharge to the solid sample under supersonic expansion and its photoelectron spectrum was recorded after mass selection. The vertical detachment energy of Alq3⁻ and the adiabatic electron affinity of Alq3 were determined to be 1.24 ± 0.01 and 0.89 ± 0.04 eV, respectively. By using these energies determined for monomeric Alq₃, the reorganization energy for the intermolecular electron transport in bulk Alq₃ was estimated to be 0.70 \pm 0.08 eV.



1. INTRODUCTION

Organic semiconductors are widely used in various devices including organic light-emitting diodes,¹ organic photovoltaics,² and organic field-effect transistors.³ However, the performance of electron transport materials (ETMs) is more difficult to predict than that of hole transport materials because electron affinity in the solid phase (EA_{bulk}), a key descriptor of the electron transport properties, cannot be determined precisely. To circumvent the problems, much effort has been made to directly determine the EA_{bulk} value using inverse photoelectron spectroscopy (IPES)^{4,5} on a film and photoelectron spectroscopy (PES) on a negative ion on the film. However, the EA_{bulk} values determined by these methods are significantly different: the EA_{bulk} values of tris(8-hydroxyquinolinato)aluminum (Alq₃; Scheme 1), for example, were determined to be 2.06° and $\sim 2.5 \text{ eV}^7$ by IPES and PES, respectively. This discrepancy is partly due to the difference in the measurement schemes. IPES gives the vertical energy required to attach the electron to a relaxed molecule in the film, whereas PES gives the vertical energy to remove the electron from the relaxed anion in the solvation shell.

The EA_{bulk} can be estimated by an indirect method based on the EA value of the constituent monomer (EA $_{mono})\!\!:$ the EA $_{bulk}$ is estimated by stabilizing the EA_{mono} by the polarization energy and intermolecular electronic coupling.^{8,9} The EA of a

Scheme 1. (a) Meridional and (b) Facial Isomers of Alg₂; Color Codes: Pink (Al); Red (O); Blue (N); Black (C); and Gray (H)



monomer molecule is determined by PES of the corresponding molecular anion in the gas phase. PES on size-selected cluster anions of molecules also provides a novel opportunity to probe the evolutional behavior of the unoccupied states as a function of the numbers of the constituent molecules.¹

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Figure 1. (a) Negative ion mass spectrum of the anionic species generated by the PDN source and (b) photoelectron spectrum of mass-selected Alq_3^- .

The first aim of this study is to develop a new production method of a molecular anion from the solid sample for the PES experiment. The second aim is to determine experimentally the vertical detachment energy (VDE) of Alq_3^- and the adiabatic electron affinity (AEA) of Alq_3 . Then, the PES results on the Alq₃ monomer were used to estimate the reorganization energy for the intermolecular electron transport in bulk Alq_3 (λ_{bulk}) following the previous treatment applied for electron transfer (ET) between Fe ion complexes in solution¹¹ and hole transport properties of solid materials.^{10,12} These results are compared with those of theoretical calculations. Finally, we discuss reliability of the EA_{bulk} values previously reported^{6,7} by comparing the polarization energies of the Alq₃⁺ cation and the Alq₃⁻ anion.

2. RESULTS AND DISCUSSION

2.1. AEA and VDE. Figure 1a shows a typical mass spectrum of anionic species of Alq₃. Figure 1a exhibits the mass peaks for the parent ion Alq_3^- and the fragment ion Alq_2^- . This result demonstrates that the pulsed discharge nozzle (PDN) is a convenient tool for desorbing intact molecular anions from the solid samples. Figure 1b shows the photoelectron spectrum of Alq₃⁻ and exhibits a single peak at ~ 1.2 eV: the VDE value corresponding to the peak top was determined to be 1.24 ± 0.01 eV by fitting three independent spectra with a Gaussian function. The AEA value corresponding to the spectral onset could not be determined unambiguously because the (0, 0) origin peak is not visible in the spectrum. Thus, the AEA value was determined to be 0.89 ± 0.04 eV by the energy at which the second derivative of the spectrum took a local maximum. The AEA of solid Alq₃ $(2.06 \text{ eV})^5$ and photoemission threshold from the Alq₃⁻ anion located on the surface of Alq₃ $(2.5 \text{ eV})^6$ are significantly larger than that of the Alq₃ monomer mainly due to the polarization energy.

The structures of the meridional and facial isomers of neutral Alq₃ in singlet states (1 and 2, respectively) and anionic Alq₃⁻ in doublet states (3 and 4, respectively) were optimized. The atomic coordinates of 1-4 are listed in Table S1, and the relative stabilities between the isomers are compared in Table 1. For neutral Alq₃, meridional isomer 1 is more stable than facial isomer 2 by 0.24 eV. This result is consistent with the fact that Alq₃ molecules in the commercially available reagents are in the meridional form.¹³ In the anionic state, meridional isomer 3 was also more stable than facial isomer 4 by 0.26 eV. The higher stability of meridional isomers both in neutral and anionic states strongly suggests that Alq₃⁻ in our beam takes

Table 1. Experimental and Theoretical Comparison of VDE of $\rm Alq_3^-$ and AEA and VEA of $\rm Alq_3$

structure	ΔE (eV)	VDE (eV)	AEA (eV)	VEA (eV)		
1	0		1.02	0.90		
2	0.24 ^{<i>a</i>}		1.00	0.93		
3	0	1.18				
4	0.26 ^b	1.06				
Exp ^c		1.24 ± 0.01	0.89 ± 0.04			
With respect to 1. ^b With respect to 3. ^c This study.						

meridional form 3. The AEA value of 1 was calculated as the energy difference between 1 and 3 and that of 2 was calculated as the energy difference between 2 and 4. The experimental AEA value ($0.89 \pm 0.04 \text{ eV}$) is similar to that calculated for 1 (1.02 eV) (Table 1). The VDE values of 3 and 4 were calculated to be 1.18 and 1.06 eV (Table 1), respectively, from the energy differences between the corresponding neutral states with the geometries of 3 and 4. The experimental VDE value ($1.24 \pm 0.01 \text{ eV}$) is comparable to that predicted for 3 (1.18 eV). The vertical electron affinities (VEAs) of 1 and 2 were calculated from the energy difference between the corresponding anionic states with the geometries of 1 and 2, respectively. The VEA values of 1 and 2 (Table 1) are similar to those reported previously (0.95 and 0.94 eV, respectively).¹⁴

2.2. Reorganization Energy. The electron transporting properties of ETMs are described by a simple ET model, in which the electron localized at a certain molecule hops to the neighboring molecule. Within the framework of this hopping model, the rate constant *C* for ET is given by the following formula^{15,16}

$$C = \sqrt{\pi/\lambda kT} \left(V^2/\hbar \right) \exp(-\lambda/4kT) \tag{1}$$

where k, \hbar , T, V, and λ represent the Boltzmann constant, the reduced Planck constant, temperature, electronic coupling matrix element, and reorganization energy, respectively.¹⁶ Equation 1 predicts that the ET rate increases with a decrease in λ , indicating that the estimation of reorganization energy λ is a key for rational development of useful ETMs.

We herein applied a simple method for estimating the λ_{bulk} value for the intermolecular ET in a solid of molecule M.¹⁷ Figure 2a shows the schematic potential curves for ET from the anion M⁻ to an adjacent M in the bulk film that accompanies the change in inter- and intramolecular structures from geometry X to Y. Because this ET process is thermoneutral, λ_{bulk} corresponds to the energy required for the ET from M⁻ to another M while retaining both inter- and



Figure 2. Potential energy surfaces associated with (a) the intermolecular ET in the film of M and (b) electron attachment to M and detachment from M⁻. Red triangles and blue spheres represent M⁻ and M in their most stable structures, respectively. Blue triangles (M*) and red spheres (M^{-*}) represent the neutral molecule with the same geometry as the ground state of M⁻ and the anionic molecule with the same geometry as the ground state of M. VDE: vertical detachment energy; VEA: vertical electron affinity; AEA: adiabatic electron affinity.

intramolecular structures at geometry X. Namely, the λ_{bulk} value is given by

$$\lambda_{\text{bulk}} = \text{VDE}_{\text{bulk}} - \Delta E \tag{2}$$

where VDE_{bulk} is the energy required to remove an electron from M⁻ in the bulk to vacuum leaving internally excited M* at fixed geometry X. ΔE is the energy gained by the electron attachment to a molecule M adjacent to M* at fixed geometry X. The energy gap ΔE is approximated by the energy gained by the electron attachment to M in the bulk at the relaxed geometry (VEA_{bulk}), if we assume that the stabilization energies due to the structural relaxation of M* and to the rearrangement of the intermolecular structure are the same before (δ_1) and after (δ_2) the electron attachment (eq 3).¹⁶ λ_{bulk} is further approximated by the difference between VDE and VEA of the monomer M because the cohesion energies before and after the ET at geometry X are considered to be nearly the same (eq 4).

$$\lambda_{\text{bulk}} \approx \text{VDE}_{\text{bulk}} - \text{VEA}_{\text{bulk}}$$
 (3)
 $\approx \text{VDE} - \text{VEA}$ (4)

However, the VEA value cannot be determined experimentally when it has a positive value.¹⁸ It is clear from Figure 2b that the difference between VDE and VEA in eq 4 is given by the summation of the relaxation energy of M* after electron detachment from M⁻ (δ_n) and that of M^{-*} after electron attachment to M (δ_a) (eq 5). When the structures of M and M⁻ are similar, δ_a and δ_n are approximated to be equal (eq 6).¹¹ In this case, the λ_{bulk} value is given in terms of VDE of M⁻ and AEA of M as shown in eq 7.

$$\begin{split} \lambda_{\text{bulk}} &\approx \delta_{\text{a}} + \delta_{\text{n}} \qquad (5) \\ &\approx 2\delta_{\text{n}} \qquad (6) \\ &= 2(\text{VDE} - \text{AEA}) \quad (7) \end{split}$$

Namely, the amplitude of λ_{bulk} reflects the difference between the stable structures in neutral and anionic states of the corresponding monomer as can be seen from Figure 2b. The λ_{bulk} value of Alq₃ was experimentally determined from eq 7 to be 0.70 \pm 0.08 eV. This λ_{bulk} value is most probably

overestimated because the AEA value in eq 7 was underestimated because of tailing of the spectral profile toward lower binding energy because of a limited resolution of the spectrometer. The validity of the approximation made in eq 7 was confirmed by the similarity in the $\lambda_{
m bulk}$ values of calculated for Alq₃ (1) using eqs 4 and 7; 0.28 and 0.33 eV, respectively. The λ_{bulk} value of meridional Alq₃ was reported to be 0.276 eV by density functional theory (DFT) calculation at the B3LYP/6-31G* level.¹³ According to Figure 2b, the small λ_{bulk} value is associated with the small structure change upon electron attachment to meridional Alq₃ and detachment from meridional Alq₃⁻. This interpretation is supported by significant overlap of structures of 1 and 3 (Figure S1). Structure analysis revealed that the difference in the Al–O and Al-N bond lengths is 5% at the most and that the major difference is the angle of a single ligand. The experimental λ_{bulk} value (0.70 \pm 0.08 eV) is larger than the calculated value (0.33 eV). However, it is beyond the scope of this study to discuss which λ_{bulk} value determined experimentally or theoretically is more reliable and is closer to the true λ_{bulk} value.

Finally, the λ_{bulk} values for other ETMs were estimated using eqs 4 and 7 and are listed in Table 2. The structural formulae

Table 2. λ_{bulk}	Values	Calculated	for	Various	ETMs (in eV	7)

ETMs	VDE	AEA	VEA	$\lambda_{ m bulk}^{a}$	$\lambda_{\mathrm{bulk}}^{b}$	
BBDDS	1.40	1.18	0.95	0.46	0.45	
BCP	0.83	0.62	0.40	0.43	0.41	
BtBBT	1.66	1.44	1.24	0.42	0.43	
DPP	1.20	1.13	1.07	0.13	0.13	
Liq	0.33	0.31	0.28	0.05	0.06	
PPCPD	1.06	0.81	0.48	0.58	0.51	
PTCDA	3.30	3.17	3.04	0.26	0.26	
t-Bu-PBD	1.12	0.96	0.79	0.33	0.33	
TPT	1.14	1.01	0.88	0.26	0.27	
${}^{a}\lambda_{\text{bulk}} = \text{VDE} - \text{VEA.} \; {}^{b}\lambda_{\text{bulk}} = 2(\text{VDE} - \text{AEA}).$						

and atomic coordinates of the optimized geometries for anionic and neutral states are listed in Tables S2–S10. Overall, the λ_{bulk} values are small (<~0.5 eV) because of the similarities in the structures of anions and neutrals. The results of Table 2 support that small λ_{bulk} values are fundamental requirements for efficient electron transportation.

Finally, we discuss reliability of the EA_{bulk} values reported previously [2.06 (LEIPS),⁶ 2.5 (anion PES),⁷ and 3.27 eV (optical gap)⁶ by considering the polarization energies of the Alq_3^+ cation and the Alq_3^- anion, P_+ and P_- , respectively. As discussed in ref 9, P_+ and P_- are stabilization energies of Alq₃ ions with surrounding Alq₃ molecules mainly via chargepermanent dipole (electrostatic) and charge-induced dipole (electronic polarization) interactions. We can approximate that P_+ and P_- are nearly equivalent because the permanent dipoles of Alq₃ molecules are oriented randomly in the amorphous film. Under such approximation, the P_+ value is calculated to be 1.8 eV from the difference of the ionization energy of the bulk film $(5.45 \text{ eV})^{19}$ and that of the isolated monomer (7.25 eV).²⁰ In contrast, the P_{-} values estimated from the difference between EA_{bulk} and EA_{mono} (0.89 eV) are 1.2, 1.6, and 2.4 eV when the values of 2.06, ⁶ 2.5, ⁷ and 3.27 eV⁶ are used as EA_{bulk} , respectively. We conclude from the comparison between P_+ and P_{-} that the EA_{bulk} value determined by the anion PES' is more reasonable than those determined by LEIPS or optical gap.



Figure 3. Schematic diagram of apparatus. Inset shows a PDN source.

3. CONCLUSION

PES was applied on a mass-selected beam of a molecular anion of tris(8-hydroxyquinolinato)aluminum (Alq₃) generated by a PDN. The VDE of Alq3⁻ and the AEA of Alq3 were determined to be 1.24 ± 0.01 and 0.89 ± 0.04 eV, respectively. We estimated the reorganization energy for the electron transport in the bulk Alq₃ (λ_{bulk}) based on the AEA and VDE values of the corresponding monomer. Two assumptions made for this estimation were: (1) the relaxation energies for the photodetached neutral Alq₃^{*} are the same regardless whether the solvation shell contains the Alq_3^- anion or not; (2) the relaxation energy of the Alq₃ monomer after photodetachment and that of the Alq₃⁻ anion after the electron attachment are the same. The λ_{bulk} value estimated based on the PES data of Alq_3^- was 0.70 \pm 0.08 eV, whereas the theoretical calculations gave a value of 0.33 eV. The λ values theoretically estimated for various ETMs were in the range of 0.05–0.6 eV, reflecting a small structural change upon electron attachment to and detachment from these molecules.

4. METHODS

4.1. Experimental Section. Figure 3 shows a schematic diagram of the experimental apparatus. The apparatus consists of a PDN^{21-23} modified for solid samples, a time-of-flight mass spectrometer (TOF-MS), and a magnetic bottle-type photo-electron spectrometer (MBPS).^{24–26} The anion of Alq₃ was generated using a PDN (inset, Figure 3). The PDN was operated by applying a pulsed voltage (-1 to -2 kV, 10 Hz) to the cathode onto which the solid sample of Alq₃ was deposited under the pulsed expansion of Ar gas (purity: >99.999%) with a stagnation pressure of ~0.2 MPa. The product anions were extracted perpendicularly to the initial beam direction by applying a pulsed electric field to the grids, and then were accelerated to 3 keV, and analyzed by the TOF-MS. The Alq₃⁻ thus produced was mass-separated and introduced to the MBPS, and then irradiated by an unfocused second harmonics output from an Nd:YAG laser (532 nm). The photoelectrons were detected using a micro-channel plate. The photoelectron spectra were obtained by the accumulations of 80 000 laser shots and were smoothed by averaging the photoelectron counts of ten neighboring points after background subtraction. The binding energies of the photoelectrons were calibrated against the photoelectron spectrum of I⁻ obtained by using the

fourth harmonics output from an Nd:YAG laser (266 nm). The energy resolution of the MBPS was 65 meV at a kinetic energy of 1 eV.

4.2. Computational Section. Alq₃ has two isomers: a meridional isomer with C_1 symmetry and a facial isomer with C_3 symmetry (Scheme 1). Three oxygen and three nitrogen atoms of the quinoline ligands are located on opposite ridges of the octahedron in the former, whereas they form opposing faces of the octahedron in the latter. Electronic and geometric structures of two isomers of Alq₃⁻ and Alq₃ were calculated by DFT at the level of B3LYP/6-311++G(d,p) using the Gaussian 09 program.²⁷ The AEA value of Alq₃⁻ and Alq₃ at their most stable structures. The VDE value of Alq₃⁻ was obtained by subtracting the energies from those of the corresponding neutral state with the identical geometries. Zero-point corrections were not conducted.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsome-ga.8b02206.

Comparison of structures of 1 and 3, three-dimensional coordinates of optimized structures of 1-4, abbreviated names and three-dimensional coordinates of optimized structures of ETMs listed in Table S2 (PDF)

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Notes

The authors declare no competing financial interest.

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