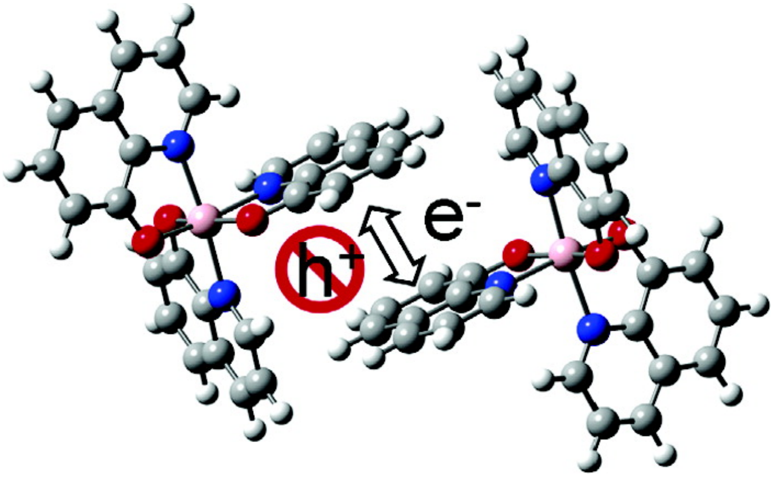
Communication

Charge Transport Properties of Tris(8-hydroxyquinolinato)aluminum(III): Why It Is an Electron Transporter

Bo Chao Lin, Cheu P. Cheng, Zhi-Qiang You, and Chao-Ping Hsu

J. Am. Chem. Soc., **2005**, 127 (1), 66-67• DOI: 10.1021/ja045087t • Publication Date (Web): 13 December 2004



J|A|C|S
COMMUNICATIONS

Charge Transport Properties of Tris(8-hydroxyquinolinato)aluminum(III): Why It Is an Electron Transporter

Bo Chao Lin,[†] Cheu P. Cheng,*[,†] Zhi-Qiang You,[‡] and Chao-Ping Hsu*[,‡]
Department of Chemistry, National Tsing Hua University, Kuang-Fu Road, Hsinchu, 300, Taiwan, and
Institute of Chemistry, Academia Sinica, 128 Sec. 2, Academia Road, Nankong, Taipei 115, Taiwan

Received August 16, 2004; E-mail: cpcheng@mx.nthu.edu.tw (C.P.C.); cherri@chem.sinica.edu.tw (C.-P.H.)

Charge transport in organic materials is one of the most important properties in the performance of organic light-emitting diode (OLED),[1] organic field effect transistor,[2] and organic solar cell.[3] For OLEDs, the location of the electron−hole recombination zone where excitons are created and light is emitted is directly affected by the mobilities of electrons and holes in the materials. This location and the conditions of exciton formation have a great influence on the efficiency of OLED.[4] High charge mobilities also reduce resistance of devices, leading to higher efficiency. Despite the importance of charge transport, our understanding of this process is still rudimentary.[5] Insight into the charge transport phenomenon in solid state could establish general guidelines in designing materials with desirable charge transport properties. As a first step toward this goal, we investigated the charge transport properties of tris(8-hydroxyquinolinato)aluminum(III), Alq, the most extensively used electron transport material in OLEDs. Alq was initially discovered by trial and error. The reason this material exhibits better electron mobility than hole mobility has remained illusive. In this communication, we show that the charge-transfer integrals for electron transport can be more than 10 times over those for hole transport because of the presence of effective LUMO overlaps between neighboring molecules and the absence of effective HOMO overlaps. This difference predicts a 2 orders of magnitude higher mobility for electron than for hole in Alq.

The charge mobilities in molecular organic materials can be described by the band theory[6] or the hopping model.[7] In the former, the conduction of charge through bands formed by the overlapping MOs between neighboring molecules is an activationless process. The latter is suitable when couplings between neighboring molecules are small and conduction is an activation process.[8] For most thin-film amorphous materials in OLED, the intermolecular interactions are weak, and therefore the hopping model is appropriate. In this model, the charge transport process can be divided into two parts: (1) an intermolecular process in which charge hops between two molecules and (2) the macroscopic hopping pathway in which the intermolecular processes are combined to form a conducting pathway. This communication addresses the intermolecular process. The rate of intermolecular electron hopping can be described by the Marcus theory given in eq 1.[7g]

$$k_{\mathrm{et}} = \frac{2\pi}{\hbar}\frac{{H_{\mathrm{da}}}^2}{\sqrt{4\pi\lambda kT}}\exp -\frac{(\Delta G^0+\lambda)^2}{4\lambda kT} \qquad (1)$$

Here, λ is reorganization energy, H_{da} is charge-transfer integral, and ΔG^0 is the free energy difference between the donor−acceptor or the hopping partners.

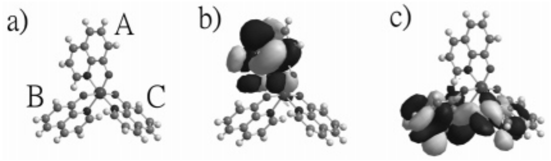


Figure 1. (a) Structure, (b) HOMO, (c) LUMO of *mer*-Alq.

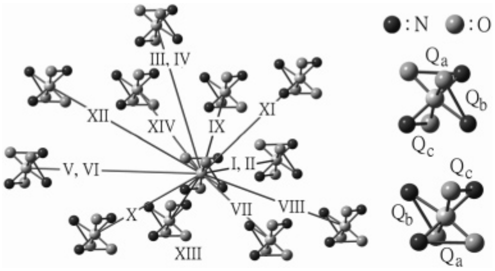


Figure 2. All charge hopping pathways for a particular Alq molecule.

The reorganization energy λ consists of contributions from the inner reorganization energy λ_i and the external polarization λ_o. λ_o may be in the range 1.0−1.5 eV reported for the polyacenes.[5a] λ_i is an intramolecular property in nature that can be evaluated by quantum chemistry calculation.[7e,9] We carried out DFT-B3LYP calculations on *mer*-Alq, which is the isomer existing in OLED devices,[10] employing a 6-31 G* basis set using the Gaussian 98 program suite. Our calculation yielded λ_i (h) = 0.242 eV and λ_i (e) = 0.276 eV(Supporting Information). The slightly smaller λ_i (h) would suggest that Alq is a better hole than electron transporter, apparently contradicting the experimental observations.[11] This suggests that the electronic coupling factor H_{da} must influence charge transport in a major way.

Since the MOs of Alq play a vital role in charge transport, we carried out HF/6-31G* calculations on *mer*-Alq[12] with the experimental geometry.[10] The results (Figure 1) show that HOMO is largely localized on q_a and LUMO is on q_b with some contribution from q_c.

The relative positions of the two molecules in the hopping complexes are necessary for calculating H_{da} for *mer*-Alq in an amorphous film. An amorphous material can be considered as a collection of molecules with relative positions similar to that in crystalline state without long range order. Among the reported structures of Alq,[10] only four solvent-free phases[10c,d] are known: α-, β-phase, and high-temperature (>380 °C) δ- and γ-phase. The β-phase is more densely packed than the α-phase. The UV−vis and fluorescence spectra in the amorphous film are closer to that in the β-phase than in the α-phase.[10c] Therefore, the β-phase is our choice in simulating the relative positions of pairs of Alq. Alq in the β-phase has a space group $P\bar{1}$; each unit cell has two molecules related by inversion symmetry. A charge on an Alq molecule can hop to others related by translational symmetry in neighboring unit cells, as shown in pathways I−VI in Figure 2. The charge can also hop to other molecules related by inversion symmetry in addition to translational symmetries in neighboring unit cells as in pathways VII−XIV in Figure 2.

[†] National Tsing Hua University.
[‡] Academia Sinica.

10.1021/ja045087t CCC: $30.25

Table 1. Charge Transfer Integrals H_{da}(h) for Hole and H_{da}(e) for Electron between an Alq Molecule at Unit Cell (0,0,0) with Al Coordinates at (0.2229, − 0.1942, 0.2404) in Crystal Axis System and Its Neighbors[a]

pathway	I, II	III, IV	V, VI	VII	VIII	IX	X	XI	XII	XIII	XIV
partner[b]	(±1,0,0)	(0,±1,0)	(0,0,±1)	(0,0,0)	(1,0,0)	(0,−1,0)	(0,0,1)	(1,−1,0)	(0,−1,1)	(1,0,1)	(1,−1,1)
Al−Al/Å	8.443	10.252	13.171	8.957	10.070	7.914	8.101	9.112	11.579	7.710	11.275
contact[c]	$H2_c$−$C3_a$	$H6_a$−$C7_c$	$H6_b$−$H7_a$	$C9_b$−$C9_b$	$C3_b$−$C3_b$	$C7_a$−$H6_b$	$C2_c$−$C5_c$	$C3_a$−$C3_a$	$H7_a$−$C2_c$	$C9_a$−$H6_c$	$H6_a$−$H7_a$
H_{da}(h)/10^{-4} eV	24.6[d]	3.99[d]	0.0030[d]	3.40	0.408	49.4	33.2[d]	31.3	1.50	121	159
H_{da}(e)/10^{-4} eV	2.83[d]	11.8[d]	0.0037[d]	2890[d]	1940[d]	2.99	20.8	83.7	0.544	30.5	0.136

[a] Al−Al distances and contacts in hopping complex are also given. [b] The unit cell where the hopping partner is located. [c] Atoms of closest contact between neighboring Alq molecules in each pathways; subscripts denote the particular ligand involved in the contact. [d] Results of DC coupling calculation

We calculated H_{da} employing either Koopmans Theorem in conjunction with Hartree−Fock model (HF−KT)[13] or the direct coupling scheme.[14−16] HF−KT results were obtained via HF/6-31 G*(Gaussian 98) calculations of the neutral hopping complexes. Energy splitting values were calculated as the energy differences between HOMO and HOMO−1 (for hole transfer) or between LUMO and LUMO+1 (for electron transfer) of the hopping complex. H_{da} is half of the energy splitting. The HF−KT scheme sometimes fails,[13] as indicated by distorted HOMO or LUMO that are no longer simple linear combination of charge-localized orbitals. For these cases, we report results obtained from the direct coupling (DC) scheme.

The magnitudes of H_{da}'s (Table 1) are about one to several orders of magnitude less than the value of λ. According to KT, good overlap of the HOMOs and LUMOs of the two interacting partners naturally leads to a large value for H_{da}(h)/H_{da}(e). When the Al−Al distance between hopping partners is large, there is poor overlap of orbitals and consequently small H_{da} values, such as in pathways V, VI, and XII. From the HOMO and LUMO plots of Alq in Figure 1, one expects H_{da}(h)(H_{da}(e)) to be large when overlap of π-orbitals on the q_a(q_b and q_c) of hopping partners is good.

Examination of the geometries of the hopping pairs (Supporting Information) reveals that there are two types of molecular contacts among all pathways: (i) the two q planes are parallel to each other (pathways VII, VIII, X, XI, and XIV) and (ii) the two q planes deviate significantly from being parallel (all other pathways). One can easily envisage that the parallel configurations may yield larger overlap than the nonparallel types. Indeed, the parallel q_b's in pathways VII and VIII lead to the two largest H_{da}(e). However, parallelism between the contacting q planes does not guarantee large H_{da}, because overlap in part of q may have a sign opposite to that of the other part leading to cancellation. When there is significant cancellation, we get a poor overlap and consequently small H_{da}, as in the situations of H_{da}(e) in pathway X and H_{da}(h) in pathway XI. H_{da}(h) in pathway XIV is the largest among all H_{da}(h)'s. But it is smaller by 1 order of magnitude than H_{da}(e) in VII and VIII because of the longer distances between the two q_a rings. According to eq 1, maximal k_{et} for electron transfer controlled by H_{da}(e)'s will be 2 orders of magnitude larger than that for hole transfer controlled by H_{da}(h), because of the square dependence on H_{da}. Consequently, electron mobility is predicted to be 2 orders of magnitude larger than that for hole, consistent with experimental observations.[11] Work in constructing macroscopic charge transfer pathways is currently undertaking.

In conclusion, we have shown that the charge-transfer integral H_{da} is the most crucial parameter affecting the charge transport properties of Alq. The distances and relative orientations of Alqs in 14 intermolecular hopping complexes are such that there are some complexes with effective overlap for LUMO but none for HOMO. Consequently, some H_{da}(e)'s are more than 1 order of magnitude larger than any H_{da}(h). This explains why Alq is a better electron transporter than hole transporter.

Acknowledgment. The financial support of the National Science Council of Taiwan (Grant NSC92-2113-M-007-037, NSC92-2113-M-001-035) and the Ministry of Education of Taiwan (Grant 89-FA04-AA) is appreciated.

Supporting Information Available: Reorganization energies of Alq, experimental geometries of the hopping complexes in all pathways, and the associated orbital energies of HOMOs and LUMOs. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Tang, C. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151.

(2) (a) Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 1684. (b) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. N.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685.

(3) (a) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474. (b) Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Nature* **1995**, *376*, 498.

(4) Aziz, H.; Popovic, Z. D.; Hu, N. X.; Hor, A. M.; Xu, G. *Science* **1999**, *283*, 1900.

(5) (a) Silinsh, E. A.; Cápek, V. *Organic Molecular Crystals: Interaction, Localization, and Transport Phenomena*; AIP: New York, 1994. (b) Mitschke, U.; Bauerle, P. *J. Mater. Chem.* **2000**, *10*, 1471.

(6) (a) Cheng, Y. C.; Silbey, R. J.; da Silva Filho, D. A.; Calbert, J. P.; Cormil, J.; Brédas J. *Chem. Phys.* **2003**, *118*, 3764. (b) Brédas, J. L.; Calbert, J. P.; da Silva Filho, D. A.; Cornil, J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5804.

(7) (a) Nelsen, S. F.; Trieber, D. A., II; Ismagilov, R. F.; Teki, Y. *J. Am. Chem. Soc.* **2001**, *123*, 5684. (b) Nelsen, S. F.; Blomgren, F. *J. Org. Chem.* **2001**, *66*, 6551. (c) Sakanoue, K.; Motoda, M.; Sugimoto, M.; Sakaki, S. *J. Phys. Chem. A* **1999**, *103*, 5551. (d) Malagoli, M.; Bredas, J. L. *Chem. Phys. Lett.* **2000**, *327*, 13. (e) Li, X.-Y.; Tong, J.; He, F.-C. *Chem. Phys.* **2000**, *260*, 283. (f) Lin, B. C.; Cheng, C. P.; Lao, Z. P. *J. Phys. Chem. A* **2003**, *107*, 5241. (g) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(8) (a) Silinsh, E. A.; Klimkāns, A.; Larsson, S.; Čápek, V. *Chem. Phys.* **1995**, *198*, 311. (b) Larsson, S.; Braga, M. *Chem. Phys.* **1993**, *176*, 367.

(9) (a) Johansson, N.; Osada, T.; Stafstrom, S.; Salaneck, W. R.; Parente, V.; dos Santos, D. A.; Crispin, X.; Bredas, J. L. *J. Chem. Phys.* **1999**, *111*, 2157. (b) Kushto, G. P.; Iizumi, Y.; Kido, J.; Kafafi, Z. H. *J. Phys. Chem. A* **2000**, *104*, 3670. (c) Martin, R. L.; Kress, J. D.; Campbell, I. H.; Smith, D. L. *Phys. Rev. B* **2000**, *61*, 15804. (d) Halls, M. D.; Schlegel, H. B. *Chem. Mater.* **2001**, *13*, 2632.

(10) (a) Schmidbaur, H.; Lettenbauer, J.; Wilkinson, D. L.; Müller, G.; Kumberger, O. Z. *Z. Naturforsch.* **1991**, *B46*, 901. (b) Fujii, I.; Hirayama, N.; Ohtani, J.; Kodama, K. *Anal. Sci.* **1996**, *12*, 153. (c) Brinkmann, M.; Gadret, G.; Muccini, M.; Taliani, C.; Mascinocchi, N.; Sironi, A. *J. Am. Chem. Soc.* **2000**, *122*, 5147. (d) Cölle, M.; Gmeiner, J.; Milius, W.; Hillebrecht, H.; Brütting, W. *Adv. Funct. Mater.* **2003**, *13*, 108.

(11) Naka, S.; Okada, H.; Onnagawa, H.; Yamaguchi, Y.; Tsutsui, T. *Synth. Met.* **2000**, *111−112*, 331.

(12) Sugimoto, M.; Sakaki, S.; Sakanoue, K.; Newton, M. D. *J. Appl. Phys.* **2001**, *90*, 6092.

(13) (a) Jordan, K. D.; Paddon-Row, M. N. *J. Phys. Chem.* **1992**, *96*, 1188. (b) Liang, C.; Newton, M. D. *J. Phys. Chem.* **1992**, *96*, 2855. (c) Curtiss, L. A.; Naleway, C. A.; Miller, J. R. *J. Phys. Chem.* **1993**, *97*, 4050. (d) Rodriguez-Monge, L.; Larsson, S. *Int. J. Quantum Chem.* **1997**, *61*, 847. (e) Li, X.-Y.; Tang, X.-S.; He, F.-C. *Chem. Phys.* **1999**, *248*, 137. (f) Lu, S.-Z.; Li, X.-Y.; Liu, J.-F. *J. Phys. Chem. A* **2004**, *108*, 4125.

(14) (a) You, Z.-Q.; Shao, Y.; Hsu, C.-P. *Chem. Phys. Lett.* **2004**, *390*, 116.

(15) We employed a developmental version of Q-Chem program to perform the DC calculations. Kong, J. et al. *J. Comput. Chem.* **2000**, *21*, 1532.

(16) (a) Ohta, K.; Closs, G. L.; Morokuma, K.; Green, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 1319. (b) Farazdel, A.; Dupuis, M.; Clementi, E.; Aviram, A. *J. Am. Chem. Soc.* **1990**, *112*, 4206.

JA045087T