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Link between hopping models and percolation scaling laws for charge transport in mixtures of small molecules

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Mixed host compositions that combine charge transport materials with luminescent dyes offer superior control over exciton formation and charge transport in organic light emitting devices (OLEDs). Two approaches are typically used to optimize the fraction of charge transport materials in a mixed host composition: either an empirical percolative model, or a hopping transport model. We show that these two commonly-employed models are linked by an analytic expression which relates the localization length to the percolation threshold and critical exponent. The relation is confirmed both numerically and experimentally through measurements of the relative conductivity of Tris(4-carbazoyl-9-ylphenyl)amine (TCTA) :1,3-bis(3,5-dipyrid-3-yl-phenyl)benzene (BmPyPb) mixtures with different concentrations, where the TCTA plays a role as hole conductor and the BmPyPb as hole insulator. The analytic relation may allow the rational design of mixed layers of small molecules for high-performance OLEDs. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4948591]

Mixed host structures have become popular in high-performance organic light emitting devices (OLEDs).1–5 Broadly defined, a mixed host adds a material dedicated to charge transport into the conventional combination of a luminescent dye and a host material. As shown in Fig. 1, the extra flexibility gained upon the addition of a third material allows tailoring of charge balance within the emissive layer, the generation of a broad exciton recombination zone,1 and control over exciplex formation.3 Mixed hosts are especially important for high efficiency blue OLEDs because it is difficult to synthesize high-conductivity bipolar hosts with blue or UV triplet exciton levels.6 It is necessary to understand, however, the electrical properties of dilute charge transport materials within a host. Two prior studies have measured the charge carrier mobility of the electron transport materials Tris-(8-hydroxyquinoline)aluminum (AlQ3) and bis(2-methyl-8-quinolinato)-4-phenylphenolate aluminum when mixed into N,N'-di(naphthalen-1-yl)-N,N'-diphenyl-benzidine.7,8 It was observed that increasing the fraction of the conductive material leads to a higher mobility, but no clear relation between concentration and mobility was identified. Subsequently, it was observed that the electrical properties of 4,7-diphenyl-1,10-phenanthroline (BPhen)/ tetracyanoquinodimethane (TCNQ) and AlQ3/4,4′-bis(carbazol-9-yl)-biphenyl (CBP)10 mixed layers could be explained with an empirical scaling law:

\[ \sigma \propto (x - x_0)^t \]  

where \( \sigma \) is conductivity, \( x \) is the fraction of the transport material in the host, \( x_0 \) is the percolation threshold, and \( t \) is the critical exponent.11 Although the physical meaning of \( x_0 \) and \( t \) is not clear,
FIG. 1. Schematic diagram of charge transport in mixtures of small molecules: (a) below percolation threshold (b) above percolation threshold. Charge moves along a percolation path via hopping transport.

this model had been widely used to analyze charge transport in many polymer-mixture systems due to its universality and simplicity.12–17

An alternative model is based on the Miller-Abrahams (MA) model for hopping conductivity in a disordered solid:18

$$\mu \propto R^2 \exp\left(-\frac{2R}{\alpha}\right)$$ (2)

where $\mu$ is mobility, $R$ is the hopping distance, and $\alpha$ is the localization length of charge. This model has been used to determine the localization length in polymers by measuring the concentration dependence of mobility.19–22

In this work, we demonstrate analytically that Eq. (1) provides a reasonable approximation for the MA model. An expression for $\alpha$ as a function of $x_0$ and $t$ in the range $x_0 < x \leq 1$ is obtained as follows:

$$t = \frac{\partial \log(x - x_0)}{\partial \log(x)} x - x_0 = \frac{\partial \log(\rho^{-1/3}x^{-1/3})}{\partial \log(x)} \frac{x - x_0}{x} = \left(\frac{2\rho^{-1/3}x^{-1/3}}{3t} - \frac{2}{3}x^{-1}\right) \left(x^{-1} - x_0^{-1}\right)$$ (3)

where the hopping distance $R$ is $\rho^{-1/3}x^{-1/3}$ and $\rho$ is the molecular density.22 Evaluating at $x = 1$ yields:

$$\alpha \approx \frac{2(1 - x_0)}{3t + 2(1 - x_0)} \rho^{-1/3}$$ (4)

We fabricated hole-only devices to test the models against typical OLED charge transport characteristics. Figure 2(a) shows the device structure. Tris(4-carbazoyl-9-ylphenyl)amine (TCTA) is the hole-transporting material with $\rho^{-1/3} = 10.3 \text{ Å}$. 1,3-bis(3,5-dipryl-3-yl-phenyl)benzene (BmPyPb) is an electron transporting material which functions here as an insulating host; see Fig. 2(b). As shown in Fig. 2(c), 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) is used as hole-injection

FIG. 2. (a) Structure of the hole only devices. (b) Molecular structures of TCTA and BmPyPb. (c) Energy level configuration of the devices. (d) J-V characteristics of the hole only devices with different mixing ratio. Inset: Relative current density of the devices.
FIG. 3. (a) Relative current density as a function of TCTA mixing ratio. Fitting of the percolation scaling law gives the \((x_0, t)\) of \((0.18, 1.6)\). (b) Relative current density as a function of the hopping distance. Fitting with Eq. (2) gives \(\alpha\) of 2.4 Å.

Current density \(J\) –voltage \(V\) characteristics of the devices are shown in Fig. 2(d). As expected, the current density increases with the TCTA concentration. To analyze the data, we calculate the relative current density from the current density of the device divided by that of the device with a neat layer of TCTA. The results are shown inset of Fig. 2(d). Note that the relative current density is constant over driving voltages from 5.7 V to 8.7 V. The average of the relative current density in the constant region is plotted as a function of TCTA ratio, \(x\), in Fig. 3(a) and hopping distance, \(R\), in Fig. 3(b). Both models fit well. The empirical percolative model yields \((x_0, t) = (0.18, 1.6)\), and the hopping transport model fits to \(\alpha = 2.4\) Å which is similar to that obtained previously in polymers.

To analyze the robustness of the link between the hopping and empirical percolation models, we calculate the symmetric mean absolute percentage error (SMAPE) between the two models with the boundary conditions of \(x_0 + 0.05 < x < 1\) as defined in Eq. (5). The lower bound avoids the failure of the empirical percolation model at \(x = x_0\). The SMAPE along the Eq. (4) line is about 1.5 percentage points bigger. These low values for the SMAPE demonstrate the analogy between the two models and also the validity of the link described by Eq. (4).

Equation (4) could be further improved by consideration of assumptions and limitations. First, there are arguments about the coefficient of 2 in the exponential function of Eq. (2). Application of percolation theory to the MA hopping model gives a coefficient of 1.73, i.e. \(\mu \propto R^2 \exp(-1.73R/\alpha)\). We have also assumed that the transport regime is nearest-neighbor-hopping. For variable-range-hopping, the temperature and the energy levels of local molecules need...
FIG. 4. (a) Numerical calculation of the SMAPE, which is defined in Eq. (5), for the $x_0$ of 0.18. The dashed black line represents Eq. (4) (b) Extracted minimum SMAPE for $1 < t < 2.5$ from (a) (black square), and the SMAPE along the Eq. (4) in (a) (red circle). (c) The minimum SMAPE for different $x_0$ values in the range of $1 < t < 2.5$.

to be considered. To do that, we should know the density of states (DOS) of molecules. If we assume a Gaussian DOS, the standard deviation ($\sigma$) and thermal energy ($kT$) should be included in the exponential function. Nevertheless, it is valid to approximate the hopping model in the form of Eq. (2) for a limited range of $R$ with respect to $\alpha$ and $\sigma$ with respect to $kT$. Consideration of molecule’s geometry could also enhance the accuracy of the modeling. Equation (2) is based on s-type wavefunctions. For elongated molecules, Eq. (2) could be modified by using p-type wavefunctions as $\mu \propto R^4 \exp(-2R/\alpha)$. When we derive Eq. (4), we put $x = 1$ for simplicity. Further numerical calculation shows that evaluating at $x = 0.75$ gives smaller error. Moreover, it is possible to simulate the system to get ($x_0$, $t$) following previous studies that calculated $x_0$ and $t$ for a given crystal structure.

In conclusion, we have shown the analogy of hopping and percolative transport models for small molecular transport materials in mixed host layers. This verifies that the empirical percolation scaling law is a reasonable approximation of MA model for the analysis of charge transport in organic mixtures. The models were linked by a simple analytical expression that is robust across a wide range of parameters. Experimental results and numerical calculations support the result. The equation connects localization length to the percolation threshold and critical exponent, and it will help predict the electrical properties of mixtures of small molecules in practical device geometries.

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