

Electron affinity and binding energy of excitons in disordered organic semiconductors.

I. Simulation-assisted analysis of field-induced exciton dissociation experiments

E. J. de Jong¹, S. Gottardi², H. van Eersel², and R. Coehoorn^{1,3,*}¹*Department of Applied Physics and Science Education, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands*²*Simbeyond B.V., Het Eeuwsel 57, 5612 AS Eindhoven, The Netherlands*³*Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands*

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Three-dimensional kinetic Monte Carlo simulations are used to investigate the sensitivity to material parameters of the photoluminescence efficiency curves that are obtained from field-induced dissociation (FID) experiments of devices that are based on disordered small-molecule organic semiconductors. The study contains a comparison with the results of a simplified one-dimensional Master Equation model [O. Rubel *et al.*, *Phys. Rev. Lett.* **100**, 196602 (2008)] and with two-dimensional simulation results. The error-function-like efficiency curves show a field sensitivity that is strongly determined by the average exciton binding energy, $E_{\text{exc,b}}$. However, the shape of the efficiency curves is also affected by other material properties, such as the energetic disorder, the hopping attempt rate, the relative permittivity, the radiative lifetime, and various other parameters. A sensitivity analysis shows that for materials with $E_{\text{exc,b}} \approx 1.0$ eV, the results of FID experiments are nevertheless expected to enable determining $E_{\text{exc,b}}$ with an accuracy of 0.10–0.15 eV. Carrying out FID experiments is therefore expected to become a useful route to quite accurately obtain the electron affinity from the ionization energy, the optical gap, and this measured value of $E_{\text{exc,b}}$.

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I. INTRODUCTION

The functioning of organic electronic devices such as organic solar cells and organic light-emitting diodes (OLEDs) depends sensitively on the frontier orbital energies of the constituent materials. For polymer-based organic heterojunction-type organic solar cells, the driving force for charge separation is determined by the offsets of the energies of the lowest unoccupied molecular orbital (LUMO) states, E_{LUMO} , and of the highest occupied molecular orbital (HOMO) states, E_{HOMO} , of the donor and acceptor material [1]. The open circuit voltage depends on the HOMO energy of the donor and the LUMO energy of the acceptor [2]. Similarly, the device performance of OLEDs can already be affected significantly by ± 0.1 eV variations of the frontier orbital energies, e.g., due to the effects of such variations of the charge transport in mixed (host-guest) emissive layers, charge injection from the electrodes, and charge blocking at internal interfaces. Attaining a high accuracy is, in particular, a challenge for experiments that probe the LUMO energy.

Accuracy of experiments. A first difficulty of obtaining accurate frontier orbital energies is related to the structurally

disordered (amorphous) nature of organic semiconductor materials that are used in organic solar cells or OLEDs. Advantageously, amorphous materials are compatible with almost any substrate and have properties that are not affected by the presence of grain boundaries. However, a key consequence of the structural disorder is that the electron and hole states that are responsible for the charge transport are localized, instead of delocalized, and that the frontier orbital energies are expressed by distribution functions. The shape and width of the distributions functions have a strong impact on various properties, such as the charge carrier mobility [3] and the open circuit voltage of organic solar cells [4], but follow only indirectly from experiments probing such effects [5]. In addition, the presence of energetic disorder blurs the effects of energy level differences, e.g., on the rate of charge carrier injection (see, e.g., Ref. [6]), which makes an accurate determination of frontier energy levels from studies of devices containing interfaces or blended (host-guest type) materials difficult.

A second difficulty is related to the process of creating electron or hole states. Whereas we have so far used the conventional terms “HOMO energy” and “LUMO energy,” it is more correct to use the terms ionization energy (E_{IE}), defined as the smallest disorder-averaged adiabatic energy for exciting an electron from the bulk of the material to the vacuum level, and electron affinity (E_{EA}), defined as the largest disorder-averaged adiabatic energy that is gained when moving an electron from a location far away in the vacuum to the bulk of the material. The formal relationships are $E_{\text{HOMO}} = -E_{\text{IE}}$ and $E_{\text{LUMO}} = -E_{\text{EA}}$, where the frontier orbital energies

*Contact author: r.coehoorn@tue.nl

are defined relative to the vacuum level. In principle, E_{IE} and E_{EA} can be deduced from ultraviolet photoelectron spectroscopy (UPS) and low-energy inverse photoelectron spectroscopy (LEIPS) experiments [7–9], respectively, which, due to the use of low-energy electrons and a relatively narrow bandpass filter for the emitted photons, is more sensitive than conventional inverse photoelectron spectroscopy (IPES [10–12]). The accuracy with which the ionization energy can be deduced from UPS spectra is considered to be close to ~ 0.1 eV when a data analysis is made that includes the effects of the surface sensitivity of the technique, energetic disorder, a vibration-induced spectral distortion, and hole relaxation [11,13,14]. The latter two corrections compensate for the nonadiabatic character of the excitation process. The analysis of LEIPS spectra would require including the same complicating effects and should also include the effect of the more limited experimental resolution (typically 0.15–0.30 eV) and the stronger background intensity, which can even blur peak structures. So far, such a more extensive analysis has not been presented. Also analyses of the results of more indirect techniques that have been used to determine E_{EA} would require that the complications that have been mentioned above, related to the disordered nature of the materials and a certain degree of nonadiabaticity of the excitation processes, be carefully considered. Examples of such techniques include UPS of anion-containing materials after optical excitation [15] or alkali doping [16], electroabsorption spectroscopy [17–19], electron energy loss spectroscopy (EELS) [10,20], photon-energy dependent photoconduction studies [21–23], electroreflectance experiments [24], scanning tunneling microscopy (STM [25]), cyclic voltammetry (CV, with a correction for electrode and solvent screening [26]), energy-resolved electrochemical impedance spectroscopy (ER-EIS [27,28]), studies of charge-transfer state emission after blending [29], and field-induced dissociation (FID) experiments [30–39].

A third difficulty is that the localized nature of the electronic states and the small relative dielectric constant give rise to a significant exciton binding energy, $E_{exc,b}$. Depending on the molecular size, the detailed molecular structure and the nature of the exciton (singlet or triplet), various types of experiments are indicative of values of $E_{exc,b}$ up to more than 1 eV [20]. Estimating the LUMO energy by adding the measured optical gap energy to the HOMO energy leads therefore, in general, to a large error, in particular for small-molecule materials for which $E_{exc,b}$ tends to be larger than for polymers due to the stronger degree of exciton localization [20]. As the ionization energy and (singlet) optical gap energy can often be determined with an accuracy of 0.1 eV or better, it would, in principle, be possible to also determine the electron affinity with such an accuracy from a low-error measurement of the (singlet) exciton binding energy using the fundamental relation

$$E_{EA} = E_{IE} - E_{exc} - E_{exc,b}, \quad (1)$$

where E_{exc} is the adiabatic and configuration-averaged singlet exciton energy that determines the optical gap.

Paper series. This is the first of a series of three papers in which we explore various routes towards determining the electron affinity and the exciton binding energy with an accu-

racy of 0.1 eV or better. Whereas many of the earlier studies, mentioned above, were carried out for polymers, we focus here on small-molecule materials. That will allow us to make use of recently developed advanced simulation techniques that can realistically describe the molecular structure and interaction processes. In this paper (paper I), we study to what extent an analysis of FID experiments could provide values of the exciton binding energy with an accuracy of 0.1 eV or better, as would be required to obtain, using Eq. (1), the electron affinity with a similar accuracy. For that purpose, we will use three-dimensional kinetic Monte Carlo (3D-KMC) simulations to analyze the sensitivity of such experiments to a wide range of material and process parameters. In paper II, a full theoretical toolchain including molecular-dynamics-based thin-film deposition simulations, first-principles Green's function (GW) calculations of the electron affinity, and combined GW and Bethe Salpeter Equation (GW-BSE) simulations of the distribution of singlet and triplet exciton binding energies will be demonstrated [40]. The study focuses on the prototypical blue fluorescent emitter material 2-methyl-9,10-bis(naphthalen-2-yl)anthracene (MADN). In an earlier study for two (α and β) isomers of MADN, the accuracy of the theoretical value of E_{IE} was shown to be consistent within 0.1 eV with the results of UPS experiments, after including in the analysis of these experiments the effects of the surface sensitivity, energetic disorder, vibrational excitations, and hole relaxation [13]. In paper II, the theoretical electron affinity and results from LEIPS experiments for both isomers are found to be consistent, albeit that the theoretical and experimental uncertainties are larger than for the ionization energy studies in Ref. [13]. In paper III, results are presented of FID experiments for neat films of eight organic semiconductor materials that are often used in OLEDs [41]. We apply, in paper III, the theoretical findings that are presented in the present work to FID results for the two isomers of MADN, and demonstrate the practical applicability and some limitations of the methodology that is developed here.

Literature on FID. Field-induced dissociation experiments probe the electric-field-dependent decay of the total photoluminescence (PL) intensity and the accompanying increase of the photocurrent. Much early work has been done on polymers, with the purpose to obtain information about the exciton binding energy, to study the influence of FID on the efficiency roll-off of polymer OLEDs, or to deduce the formation ratio of singlet and triplet excitons in fluorescent polymer OLEDs [30–35,37,42,43], while relatively few studies have included work on small-molecule materials [36,39,42,44]. In small-molecule-based phosphorescent OLEDs, field-induced dissociation affects the efficiency roll-off [45,46]. With the advent of OLEDs that are operated at very high electric fields, e.g., in pulsed devices that show stimulated emission or lasing [47] or that can be applied for optical communication at high band widths [48], the subject remains of great current interest. Important insights concerning the electric field dependence of the FID probability were obtained by Rubel and co-workers [37], who developed an exact theoretical expression for the field-dependent emission intensity for a one-dimensional (1D) system in which electron-hole pair dissociation takes place at the (1D) interface between a donor and acceptor phase. Overcoming the Coulomb barrier was assumed to be due

to a multistep hopping process of a single carrier between molecular sites with a distribution of energies. In the absence of energetic disorder and assuming model parameters that are consistent with the assumptions made within the Onsager continuous and isotropic medium theory [49] and the Frenkel single-step dissociation theory [50], the model was shown to provide, in both cases, identical expressions for the dissociation probability. Energetic disorder was shown to lead to an enhanced or reduced dissociation probability at small and large electric fields, respectively.

This paper. Here, we study to what extent the theoretical FID curves are sensitive to the system dimension (1D, 2D, or 3D), the assumed dissociation process (dissociation of localized or charge-transfer excitons, and dissociation due to single-carrier or two-carrier hopping), and a large set of electronic and excitonic material parameters. In Ref. [37], a mean-field type of Master Equation model was used. However, in the case of dissociation due to electron *and* hole hopping, correlation effects should be taken into account. We therefore use, in such cases, a KMC model. It is known from quantum-chemical studies that the distributions of the HOMO and LUMO energies can be correlated [51]. In actual systems, all four energies in Eq. (1) can be correlated. In such a situation, Eq. (1) does not necessarily give the proper relationship between their disorder-averaged values. We study, in this paper, the sensitivity to such correlations, so that this effect can be included in paper III when comparing theoretical and experimental results for the two isomers of MADN.

The structure of this paper is as follows. In Sec. II, we describe the simulation method. Section III contains simulation results for 1D, 2D, and 3D systems, for a fixed set of material parameters. In Sec. IV, we study the sensitivity of the FID curves for 3D systems to variations of the material parameters. The feasibility of deducing $E_{\text{exc},b}$ from FID experiments with an accuracy of 0.1 eV or better is discussed in Sec. V. Section VI summarizes the results and conclusions.

II. SIMULATION METHOD

A. Basic model

We study field-induced dissociation of excitons that are at time $t = 0$ located randomly on the sites of a simple cubic lattice with a lattice constant a . The HOMO and LUMO densities of states are Gaussian, with a width (standard deviation) σ_h and σ_e , respectively. The exciton radiative lifetime is τ_{rad} . Nonradiative decay does not affect the electric field dependence of the normalized PL efficiency and is neglected. The electron and hole transfer rates from a site i to a site j are described using the Miller-Abrahams formula [52],

$$v_{i,j} = v_1 \exp \left[-\frac{2(r_{ij} - a)}{\lambda} - \frac{\Delta E_{ij} + |\Delta E_{ij}|}{2k_B T} \right], \quad (2)$$

with v_1 the hopping attempt rate to a nearest-neighbor (NN) site, r_{ij} the distance between the two sites, k_B the Boltzmann constant, T the temperature, and ΔE_{ij} the energy change upon hopping from site i to site j . ΔE_{ij} includes a contribution due to the electric field, the two disorder energies, and the change of the electron-hole interaction energy. For the initial (localized) exciton, the binding energy is $E_{\text{exc},b}$, and for

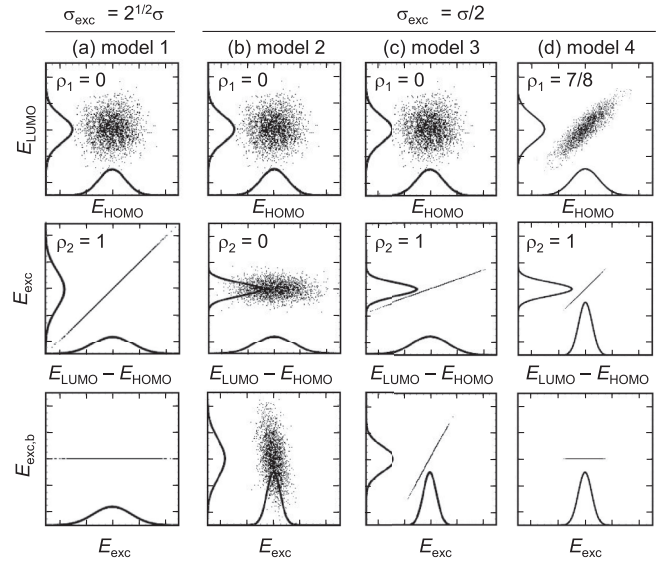


FIG. 1. (a)–(d) Correlation between the molecule-specific values of E_{HOMO} , E_{LUMO} , E_{exc} , and $E_{\text{exc},b}$ for the models 1–4 that are specified in Sec. II B. For all cases, $\sigma_h = \sigma_e = \sigma$. The boxes have a size $10\sigma \times 10\sigma$. At the outer boundaries of the figures, the distributions of the indicated quantities are shown for cases with a finite distribution width.

a charge-transfer exciton, the binding energy is $E_{\text{exc},b,\text{CT}} = e^2 / (4\pi\epsilon_0\epsilon_r r_{e-h})$, with ϵ_r the relative permittivity, e the electron charge, and r_{e-h} the electron-hole distance. The charge densities are assumed to be small, so that only geminate pair interactions play a role. The 3D-KMC simulations are carried out using the tool *bumblebee* [53]. Master Equation and KMC simulations for 1D and 2D systems are carried out using a *Mathematica* code [54].

B. Correlation between the electronic and excitonic energies

In disordered materials, the four quantities that enter Eq. (1) are all distributed. We find that the shape of FID curves depends on the correlations between these four quantities. In this section, we introduce the method that is used to parametrize these correlations. We will use, in the remainder of this paper, the less correct but more conventional frontier orbital energy nomenclature, within which Eq. (1) can be rewritten as

$$E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{exc}} + E_{\text{exc},b}. \quad (3)$$

The final simulations are performed for four specific sets of correlated distributions, called “model 1” to “model 4.” A schematic view of the energy distributions and their correlations is shown in Fig. 1. For all models, we assume $\sigma_h = \sigma_e = \sigma$. Within models 1–3, the HOMO and LUMO energies are taken to be uncorrelated. Model 1 follows the approach that has been used in many previous 3D-KMC studies of OLEDs (e.g., in Refs. [45,55,56]): $E_{\text{exc},b}$ is a fixed (site-independent) value. Within model 2, the local exciton energies are taken randomly from a Gaussian distribution with a selected width σ_{exc} . Within model 3, the local exciton energies are taken proportional to the local HOMO-LUMO gap, with a proportionality constant that assures that the exciton

energy distribution is equal to a selected width σ_{exc} . Within model 1, Eq. (3) is used to obtain the exciton energies, and within models 2 and 3, Eq. (3) is used to obtain the exciton binding energies.

In actual materials, the HOMO and LUMO energies can be correlated. Coulombic (dipolar and quadrupolar) interactions with the charge density distribution on neighbor molecules can lead to a positive correlation, whereas configurational disorder (fluctuations of dihedral bonds) can lead to a negative correlation [51]. As an example, we study, in model 4, a specific situation, viz. positively correlated HOMO and LUMO energies, local exciton energies that are proportional to the local HOMO-LUMO gap, and a fixed value of $E_{\text{exc},b}$ (as in model 1). The proportionality constant between the local exciton energies and the local HOMO-LUMO gap energies is taken such that the exciton energy distribution width is equal to a selected value σ_{exc} (as in model 3). We discuss below what HOMO-LUMO correlation is required for that purpose.

These four correlated distributions are specific cases of a general class of correlated Gaussian distributions that may be described as follows: (1) the HOMO and LUMO energies are correlated with a correlation coefficient ρ_1 , (2) the exciton energies are correlated with the HOMO-LUMO gap energy with a correlation coefficient ρ_2 , and (3) σ_{exc} is, by construction, equal to a fixed (e.g., experimental) value [57]. Distributions showing these correlations may be obtained by taking, for each site i ,

$$E_{\text{HOMO},i} = E_{\text{HOMO}} + \Delta E_{\text{HOMO},i}, \quad (4a)$$

$$E_{\text{LUMO},i} = E_{\text{LUMO}} + \Delta E_{\text{LUMO},i}, \quad (4b)$$

$$E_{\text{exc},i} = E_{\text{exc}} + \Delta E_{\text{exc},i}, \quad (4c)$$

with

$$\Delta E_{\text{HOMO},i} = \Delta E_{1,i}, \quad (5a)$$

$$\Delta E_{\text{LUMO},i} = \rho_1 \frac{\sigma_e}{\sigma_h} \Delta E_{1,i} + \sqrt{(1 - \rho_1^2)} \Delta E_{2,i}, \quad (5b)$$

$$\begin{aligned} \Delta E_{\text{exc},i} = & \rho_2 \frac{\sigma_{\text{exc}}}{\sigma_{\text{HL-gap}}} (\Delta E_{\text{LUMO},i} - \Delta E_{\text{HOMO},i}) \\ & + \sqrt{(1 - \rho_2^2)} \Delta E_{3,i}. \end{aligned} \quad (5c)$$

Here, E_{HOMO} , E_{LUMO} , and E_{exc} are the site-averaged HOMO, LUMO, and exciton energies. The energies $\Delta E_{1,i}$, $\Delta E_{2,i}$, and $\Delta E_{3,i}$ are randomly selected from Gaussian distributions with widths σ_h , σ_e , and σ_{exc} , respectively, and $\sigma_{\text{HL-gap}}$ is the width of the distribution of HOMO-LUMO gap energies,

$$\sigma_{\text{HL-gap}} = [(\rho_1 \sigma_e - \sigma_h)^2 + (1 - \rho_1^2) \sigma_e^2]^{1/2}. \quad (6)$$

The resulting width of the distribution of exciton binding energies is

$$\sigma_{\text{exc},b} = [(\rho_2 \sigma_{\text{exc}} - \sigma_{\text{HL-gap}})^2 + (1 - \rho_2^2) \sigma_{\text{exc}}^2]^{1/2}. \quad (7)$$

The correlated distributions that are assumed within model 1 are obtained when taking $\rho_1 = 0$, $\rho_2 = 1$, and $\sigma_{\text{exc}} = \sqrt{2}\sigma$ [see Fig. 1(a)]. The excitonic density of states (DOS) width is $\sigma_{\text{exc}} = (\sigma_h^2 + \sigma_e^2)^{1/2}$. For typical HOMO and LUMO disorder energies of $\sigma = 0.1$ eV, the width $\sigma_{\text{exc}} = \sqrt{2}\sigma =$

0.141 eV that is assumed within model 1 is much larger than the values of ~ 0.05 eV that follow typically from the experimental inhomogeneous broadening of PL spectra [58]. Within models 2–4, σ_{exc} can be taken equal to any selected value. We will assume that $\sigma_{\text{exc}} = \sigma/2$, i.e., a value that is close to experimental values for systems with $\sigma = 0.10$ eV.

Within model 2 [see Fig. 1(b)], ρ_1 and ρ_2 are both taken equal to zero. That leads to a relatively wide distribution of exciton binding energies ($\sigma_{\text{exc},b} = 3/2\sigma$). In paper II, this correlation type is shown to provide a fair first approximation to the results of quantum-chemical simulations for the two isomers of MADN. Within model 3, $\rho_1 = 0$ and $\rho_2 = 1$, as for model 1, but σ_{exc} is now taken to be equal to $\sigma/2$ [see Fig. 1(c)]. The resulting value of $\sigma_{\text{exc},b}$ is quite large, viz. $\sim 0.91\sigma$. Within model 4 [see Fig. 1(d)], $\rho_2 = 1$ and a fixed exciton binding energy is assumed (so that $\sigma_{\text{exc},b} = 0$). From Eqs. (6) and (7), it follows that such a situation can be obtained by taking $\rho_1 = 7/8$. We expect that future quantum-chemical simulations for realistic morphologies will clarify what types of correlations are most realistic.

C. One-dimensional reference case

When studying the sensitivity to parameter value variations, it is useful to make a comparison with the results for a simple reference case. We consider for that purpose dissociation in a 1D system within which only dissociation due to NN hopping of charge carriers of a single type is included. The electron-hole pairs are initially located on site $i = 0$. The energy of the system is then $E_0 = -E_{\text{exc},b}$, with $E_{\text{exc},b}$ the (fixed) binding energy of the localized exciton. Dissociation occurs due to NN hopping of a single charge to sites with $i \geq 0$ and is taken to be completed when the charge has reached the outer boundary of the system at site N . N is sufficiently large, so that the PL efficiency is N independent. The energy of the moving charge carrier at sites $i \geq 0$ is equal to $E_i = E_{\text{dis},i} - E_{\text{exc},b,\text{CT},i} - eiaF$, with $E_{\text{dis},i}$ the random disorder energy, $E_{\text{exc},b,\text{CT},i}$ the binding energy of the charge-transfer exciton with the moving charge on site i , and F the absolute value of the electric field. Figure 2(a) shows schematically the energy of the moving charge carrier at sites close to the origin, for $F = 0$ and for a finite value of the field, in the absence of energetic disorder. The top part of Table I gives an overview of the default parameter values for which these simulations are carried out. $E_{\text{exc},b}$ and σ will be varied. The bottom part of the table gives an overview of the other parameters that are considered in this work, and their default values when they are not varied or not specified otherwise.

From a Master Equation approach, analogous to the model developed in Ref. [37] for the case of dissociation of charge-transfer (CT) excitons, the PL efficiency is given by

$$\eta_{\text{PL}} = \frac{1/\tau_{\text{rad}}}{1/\tau_{\text{rad}} + \Gamma_{\text{diss}}}, \quad (8)$$

where the effective dissociation rate Γ_{diss} is given by

$$\Gamma_{\text{diss}} = \left[\sum_{i=0}^{N-1} \frac{1}{v_{i,i+1}} \exp\left(\frac{E_i - E_0}{k_B T}\right) \right]^{-1}. \quad (9)$$

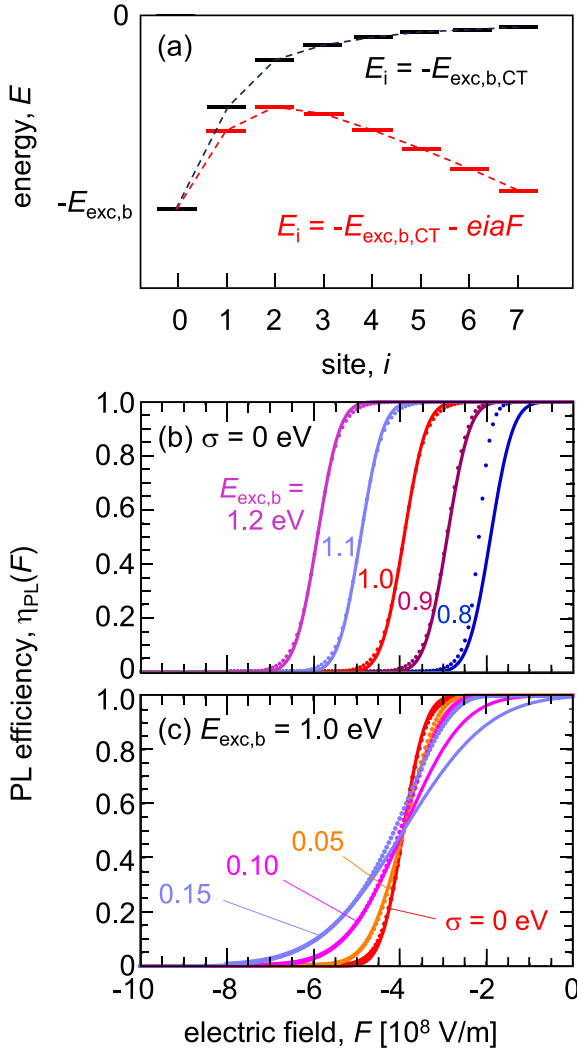


FIG. 2. (a) Schematic dependence of the total energy of an electron-hole pair for the one-dimensional reference case that has been introduced in Sec. II C. An electron-hole pair that has been created at site $i = 0$ dissociates due to hopping of one of the two charges to sites $i > 0$. The figure shows the site-dependent total energy in the absence and in the presence of an electric field. (b) Electric field dependence of the PL quantum efficiency (η_{PL}) for this model for various values of $E_{\text{exc,b}}$ with $\sigma = 0$ eV, and (c) for various values of σ with $E_{\text{exc,b}} = 1.0$ eV. The dotted curves give the exact results from Eqs. (8) and the full curves show the approximation that is given by Eq. (13) with (b) a width $\sigma_{F,0}$ [see Eq. (14)] and (c) a width $\sigma_{F,\text{tot}}$ (see the text in Sec. II C).

Here, $v_{i,i+1}$ is the hopping rate from site i to site $i+1$, given by Eq. (2). As already noted in Ref. [37], this expression shows that the effective dissociation rate is dominated by the difference between the top of the energy barrier E_i for escape and E_0 .

Useful characteristics of the function $\eta_{\text{PL}}(F)$ are the field $F_{1/2}$ at which the PL efficiency has been reduced by a factor 2 and the slope of the efficiency function at that point. For systems without disorder and with a large exciton binding energy, Eqs. (8) and (9) can be used to derive these characteristics in the following way. For systems with a sufficiently large value

TABLE I. Overview of the default set of simulation parameters used in Sec. II B (top part) and in later sections (top and bottom parts).

Parameter	Description	Value
a	intersite distance	1 nm
ν_1	hopping attempt rate	$3.3 \times 10^{10} \text{ s}^{-1}$
τ_{rad}	radiative lifetime	$1.0 \times 10^{-8} \text{ s}$
ϵ_r	relative permittivity	3.0
T	temperature	300 K
$E_{\text{exc,b}}$	exciton binding energy	1.0 eV
$\sigma_{\text{h,e}}$	disorder energy (holes, electrons)	0.10 eV
σ_{exc}	disorder energy (excitons)	0.05 eV
λ	wavefunction decay length (holes, electrons, excitons)	0.3 nm
p_{dip}	static dipole moment	0 D
R_F	Förster radius exciton transfer	0 nm

of the exciton binding energy, a hop from site 0 to site 1 will be endothermic, even for relatively large fields. However, for large fields, all forward hops from sites $i \geq 1$ are exothermic. If the field is sufficiently large, the value of Γ_{diss} at that field will be determined only by the first two terms (with $i = 0$ and $i = 1$) in the summation of Eq. (9), so that

$$\eta_{\text{PL}} \approx \left[1 + \frac{\tau_{\text{rad}} \nu_1}{2} \exp \left(-\frac{E_1 - E_0}{k_B T} \right) \right]^{-1} = \left[1 + \frac{\tau_{\text{rad}} \nu_1}{2} \exp \left(\frac{\frac{e^2}{4\pi\epsilon_0\epsilon_r a} - E_{\text{exc,b}} + eaF}{k_B T} \right) \right]^{-1}. \quad (10)$$

This leads to

$$F_{1/2} \approx \frac{1}{ae} \left[k_B T \ln \left(\frac{2}{\tau_{\text{rad}} \nu_1} \right) + E_{\text{exc,b}} - \frac{e^2}{4\pi\epsilon_0\epsilon_r a} \right] \quad (11)$$

and

$$\left. \frac{d\eta_{\text{PL}}}{dF} \right|_{F_{1/2}} \approx -\frac{ea}{4k_B T}. \quad (12)$$

The charge of the hopping particles and the sign of the field have so far been taken positive. However, in the remainder of the paper, the field will be taken negative, as in reverse bias field device experiments. We find that for large exciton binding energies, the full field dependence of η_{PL} with this convention is, to a good approximation, given by

$$\eta_{\text{PL}} \approx \frac{1}{2} \left[1 + \text{erf} \left(\frac{F - F_{1/2}}{\sqrt{2}\sigma_{F,0}} \right) \right], \quad (13)$$

where $\text{erf}(x)$ is the error function and $F_{1/2} < 0$, and with

$$\sigma_{F,0} = \frac{4k_B T}{\sqrt{2\pi} ea}. \quad (14)$$

This expression is obtained by broadening a step function at $F = F_{1/2}$ by a Gaussian with a width $\sigma_{F,0}$ that is taken such that the slope of the curve at $F = F_{1/2}$ satisfies Eq. (12).

Figure 2(b) shows that for the default parameter set that is given in the top part of Table I, this zero-disorder and

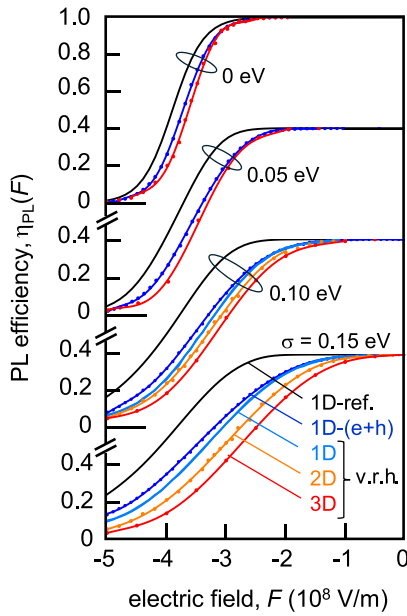


FIG. 3. Simulated FID curves for disorder energies $\sigma = 0, 0.05, 0.10$, and 0.15 eV, for a systematically varied set of simulation conditions, as discussed in Sec. III. Black curves: 1D reference case (Sec. II B). Dark blue curves: 1D system with electron and hole dissociation but only NN transfer. Light blue, orange, and red curves: 1D, 2D, and 3D systems, respectively, with electron and hole dissociation and variable-range hopping.

large binding energy approximation is excellent concerning the value of $F_{1/2}$ and the derivative at that point for $E_{\text{exc},b} = 0.9$ eV or larger. The approximation is then also quite good for smaller and larger fields. The figure shows that for $E_{\text{exc},b} = 1.0$ eV, the $F_{1/2}$ field is quite large and corresponds to an electrostatic potential energy difference between NN molecules of approximately 0.39 eV.

Figure 2(c) shows for $E_{\text{exc},b} = 1.0$ eV how the efficiency curves broaden further in the presence of energetic disorder. The curves are obtained using Eq. (8) by taking an average for a large number of spatially random disorder configurations. When the dissociation probability is only determined by the energy difference between sites 0 and 1, as assumed in the model that leads to Eq. (11), energetic disorder is expected to lead to a distribution of local values of $F_{1/2}$ with a width $\sigma_{F,\text{dis}} = \sigma/(ea)$. The full curves in the figure show how the efficiency curves are then expected to broaden, using a total width $\sigma_{F,\text{tot}} = (\sigma_{F,0}^2 + \sigma_{F,\text{dis}}^2)^{1/2}$. This approximation is excellent for small disorder energies, in particular at large fields. At large disorder energies and small fields, a high energy at sites $i \geq 2$ can oppose fast dissociation so that the actual PL efficiency is significantly larger than as predicted from the broadened error function curves.

III. SENSITIVITY TO THE SYSTEM DIMENSION AND THE HOPPING PROCESS

Figure 3 shows simulated FID curves for four values of the disorder energy, obtained by systematically varying the simulation conditions. Energy level correlation model 1 was assumed (see Sec. II B), with $\sigma_h = \sigma_e$, $\sigma_{\text{exc}} = 0.05$ eV, $\lambda =$

0.3 nm, and $E_{\text{exc},b} = 1.0$ eV. Black curves show the FID curve for the 1D reference case that was discussed in Sec. II C. Within these reference simulations, only dissociation due to NN hopping of one charge carrier was assumed. In all other simulations, hopping of both charge carriers is included. The dark blue curves show KMC simulation results for 1D systems with only NN hopping, and the light blue, orange, and red curves show KMC simulation results for 1D, 2D, and 3D systems with variable-range hopping [see Eq. (2)]. The figure shows, for this series of simulation conditions, a systematic decrease of the PL efficiency at a given field, as would be expected from the increasing number of dissociation channels. The decrease is particularly large for systems with a large energetic disorder. For $\sigma = 0.15$ eV, the value of $F_{1/2}$ that is obtained for a 3D system is 33% smaller than the value for the 1D reference case. For $\sigma \leq 0.05$ eV, the sensitivity to varying the system dimension was found to be small. For clarity, the light blue and orange curves have therefore been omitted for these two cases.

Figure 3 shows a sensitivity of $F_{1/2}$ to extending the 1D reference model (black curves) so that it includes electron *and* hole transport (dark blue curves), varying from a decrease of about 4% (no disorder) to a decrease of about 16% for $\sigma = 0.15$ eV. Within a simple model, which neglects the correlated motion of electrons and holes, one may understand this sensitivity as follows. In the absence of disorder, the inclusion of two dissociation channels, instead of one, will lead to a doubled value of the dissociation rate. From Eq. (11), a doubled value of ν_1 is expected to lead to a shift of $F_{1/2}$ by $k_B T/(a \ln 2) \approx 0.17 \times 10^8$ V/m, which indeed corresponds to a reduction of about 4%. In disordered systems, the two dissociation channels are, in general, not equivalent. In the case of strong disorder and a large field, one might expect that the dissociation process is due to either electron or hole transfer, depending on which of the two barriers formed by the first downstream neighbor molecule is smallest. The distribution of smallest energy barriers has a mean that is 0.565σ lower than that of each separate barrier [59], so that from Eq. (11) for $\sigma = 0.15$ eV, a shift of $\sim 0.8 \times 10^8$ V/m is expected. That would correspond to a reduction of about 19%, which is close to the observed value.

IV. 3D SYSTEMS: SENSITIVITY TO MATERIAL PARAMETERS

Figure 4 shows the results of 3D-KMC simulations of the sensitivity of FID curves to the average exciton binding energy and to the four correlation models that have been discussed in Sec. II B. All other parameter values are as given in Table I. The $F_{1/2}$ fields are seen to depend strongly on the value of $E_{\text{exc},b}$, even though the sensitivity is somewhat smaller than as observed for the zero-disorder 1D reference case [Fig. 1(a) and Eq. (11)]. The figure also shows that for correlation models 2–4, dissociation sets in at somewhat smaller (absolute) fields, in particular for small values of $E_{\text{exc},b}$. For large exciton binding energies, the difference between the models becomes less. We attribute that to the larger fields that are then required for dissociation, so that the relative role of differences between the distributions of energy levels becomes small. For $E_{\text{exc},b} > 1$ eV, the sensitivity to energy level correlations

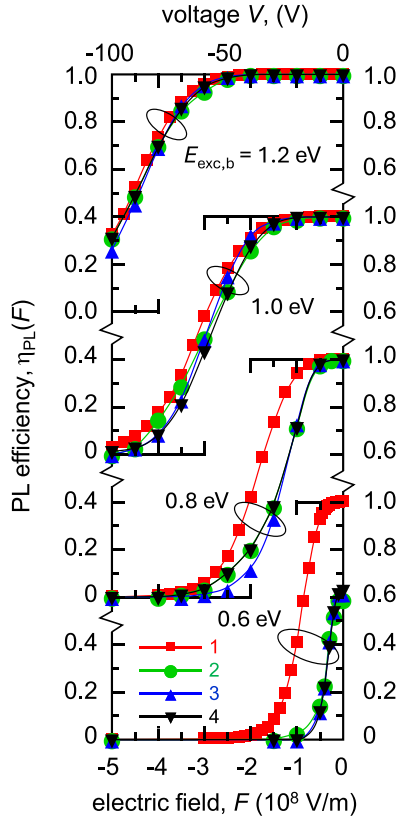


FIG. 4. Electric field dependence of the PL quantum efficiency in 3D systems, obtained from 3D-KMC simulations, for various values of the average exciton binding energy $E_{\text{exc},b}$ and for correlation models 1–4 (see Sec. II B), using the symbols that are shown in the bottom part of the figure. The other simulation parameters are given in Table I. The upper horizontal scale gives the corresponding voltage across a 200 nm device, such as studied experimentally in paper III.

becomes quite insignificant as compared to realistic experimental variabilities and parameter value uncertainties. For model 2, the FID curves (orange colored) are the least steep. We attribute that to the relatively wide exciton binding energy distribution [see Fig. 1(b)].

As a next step, we study in Fig. 5 the sensitivity to various other material parameters. The simulations are performed for a fixed value $E_{\text{exc},b} = 1.0$ eV, which is motivated by the experimental results that are presented in paper III. These show that for many materials that are used as charge transport or host materials in OLEDs the value of η_{PL} is still in the range 0.8–0.9 at $F = 0.25 \times 10^9$ V/m. Due to device breakdown, measurements at larger fields were found to be impossible with our setup and device configuration. For the set of parameters that is used in Fig. 4, that would suggest values of $E_{\text{exc},b}$ of ~ 1.0 – 1.1 eV. In view of the small sensitivity to the correlation model at such high values of $E_{\text{exc},b}$, only simulation results for model 2 are shown. The red curves in each panel of Fig. 5 show the simulation result for the set of parameters that is given in Table I. The full curves in Fig. 5(a) give a more direct comparison between the results for different values of $E_{\text{exc},b}$ than shown in Fig. 4. The dashed curves show the sensitivity to a change of the wave-function decay length λ from 0.3 to 0.1 nm. The figure shows that an uncertainty

of λ in that range would not give rise to a significant uncertainty in the value of $E_{\text{exc},b}$ that would be deduced from an FID study.

The full curves in Fig. 5(b) show the effect of a variation of the HOMO and LUMO disorder energy σ in the range 0.05–0.15 eV. The trend is similar to that shown in Fig. 3 for simulations using model 1. Some small-molecule materials that are used in OLEDs are based on molecules with large static dipole moments. A well-studied example is (2, 2', 2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBi), with dipole moments p_{dip} of (on average) 7 D [60]. In the case of a random orientation distribution, the resulting total width (standard deviation) of the DOS is [61]

$$\sigma_{\text{tot}} = \left[\sigma^2 + \left(\frac{0.0702 p_{\text{dip}} [\text{D}]}{\epsilon_r a^2 [\text{nm}^2]} \right)^2 \right]^{1/2}, \quad (15)$$

which amounts to approximately 0.19 eV for TPBi when taking σ , a , and ϵ_r from Table I. Experimental studies for TPBi, presented in paper III, indeed show much stronger FID than for materials with smaller static dipole moments. Figure 5(b) (blue dashed curve; see Ref. [62] for details on the methodology) confirms that the inclusion of 7 D dipole moments will give rise to stronger field-induced dissociation. However, the efficiency curve is closer to that for $\sigma \approx 0.15$ eV. We attribute the difference to the spatially correlated nature of dipole-moment-induced disorder, so that the actual disorder at short distances from each exciton is somewhat smaller than as expected from the total DOS width. The magenta curves in Fig. 5(b) show the sensitivity to a variation of the exciton disorder energy σ_{exc} in the range 0–0.15 eV. With increasing excitonic disorder, the slope of the efficiency curves becomes smaller. However, $F_{1/2}$ varies only a little.

Figure 5(c) shows the effect of a variation of the radiative decay rate τ_{rad} . If radiative decay and charge transfer are the only processes that are included, as in this figure, the efficiency curves are equal for equal values of $\tau_{\text{rad}} \times \nu_1$. Figure 5(c) can therefore also be viewed as a study of the dependence on the hopping attempt rate ν_1 , i.e., on the mobility. For a 1D system and for a set of specific restrictions (no disorder, only dissociation due to one charge carrier, NN hopping, relatively large binding energy, intermediate field strengths so that endothermic transfer from site 0 to site 1 is the process that determines the effective dissociation rate), Eq. (11) in Sec. II C predicts that a variation of τ_{rad} by a factor of 10 would lead to a change of $F_{1/2}$ by 0.058×10^9 V/m. The figure shows that for the 3D systems studied, the change of $F_{1/2}$ due to a 10-fold increase or decrease of τ_{rad} is quite similar, but that deviations occur for larger variations of τ_{rad} . In general, τ_{rad} is accurately known from experiment, so that the resulting uncertainty in $E_{\text{exc},b}$ will be small. However, the determination of ν_1 requires developing a mobility model using a charge transport study, which could lead to a larger uncertainty.

For small-molecule organic semiconductors, the relative permittivity ϵ_r falls typically in the range 2.5–4 [63]. Figure 5(d) shows the sensitivity to a variation of ϵ_r within that range. The accuracy with which ϵ_r can be obtained from experiment is, in general, ~ 0.3 or better. A comparison with

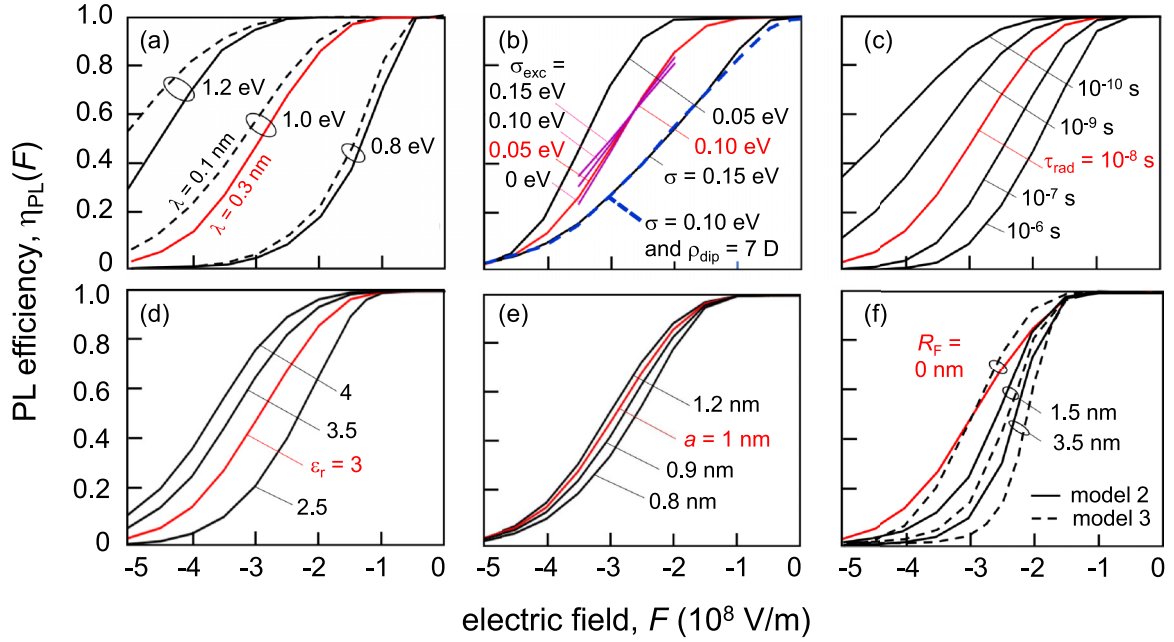


FIG. 5. Red curves: electric field dependence of the PL quantum efficiency in 3D systems, obtained from 3D-KMC simulations, for energy level correlation model 2 and for the set of simulation parameters that is given in Table I. Black and blue curves: sensitivity to a variation of one of the parameters. (a) Variation of the wave-function decay length $\lambda = 0.3$ nm (full curves) and 0.1 nm (dashed curves) for three values of the average exciton binding energy $E_{\text{exc},b}$. (b) Variation of the electronic disorder energy σ (black curves) and the excitonic disorder energy σ_{exc} (magenta curves), and an FID curve for a system in which the energy level distribution is determined by random Gaussian disorder ($\sigma = 0.10$ eV) combined with disorder due to randomly oriented molecular dipole moments of 7 D (blue dashed curve). (c) Variation of the radiative lifetime τ_{rad} . (d) Variation of the relative permittivity ϵ_r . (e) Variation of the average intersite distance a . (f) Variation of the Förster radius for exciton transfer for model 2 and model 3 systems (full and dashed curves, respectively).

the curves in Fig. 5(a) shows that such a small uncertainty would translate to only a small uncertainty in the value of $E_{\text{exc},b}$.

Within the one-dimensional reference case that has been discussed in Sec. II C, the sensitivity of the efficiency curves to the average intermolecular distance a is determined by two competing effects. On the one hand, an increase of a leads to an increase of the energy gain per hop, so that $F_{1/2}$ decreases. On the other hand, the binding energy of the charge-transfer states then decreases. The activation barrier for the first step towards dissociation then increases so that $F_{1/2}$ increases. As a result, $F_{1/2}$ varies nonmonotonically with a and shows from Eq. (11) a maximum for $a \approx 1.1$ nm, with all other parameters as given in the top part of Table I. The sensitivity of $F_{1/2}$ to a near $a = 1$ nm is therefore small. For small-molecule materials, actual values of a vary from about 0.8 to 1.1 nm [63]. Figure 5(e) shows that within that range also from full 3D-KMC simulations, only a weak sensitivity is expected.

Förster-type resonant energy transfer (FRET) of singlet excitons between equal organic donor and acceptor molecules can be characterized by a Förster radius R_F as large as 6 nm, depending on the overlap between the donor emission and the acceptor absorption spectrum [64]. Figure 5(f) shows the sensitivity to such an exciton diffusion process, for $R_F = 1.5$ and 3.5 nm with correlation model 2 (full curves) and model 3 (dashed curves). Within the simulations, the rate of isoenergetic FRET between molecules i and j at a distance r_{ij} is taken equal to $(1/\tau_{\text{rad}})(R_F/r_{ij})^6$, whereas the rate of

endothermic or exothermic FRET is treated by taking an energy difference dependence such as given in Eq. (2). For both models, FRET gives rise to enhanced field-induced dissociation. Without FRET, the efficiency curve for model 2 is somewhat less steep as for model 3. We attribute that to the wider distribution of exciton binding energies for model 2. Interestingly, FRET does not give rise to just a shift of the efficiency curves, as seen for a change of ϵ_r in Fig. 5(d), but also to an increase of their steepness. That may be understood by distinguishing two opposing effects of exciton diffusion on the effective dissociation rate. On the one hand, exciton diffusion leads to energy relaxation in the Gaussian DOS. Full relaxation shifts the average energy by $-\sigma_{\text{exc}}^2/(k_B T)$, i.e., by approximately -0.10 eV for $\sigma_{\text{exc}} = 0.05$ eV. This process, which occurs on a timescale that is independent of the field, reduces the effective dissociation rate. On the other hand, exciton diffusion also involves transfer to sites at which, due to the randomness of the system, the dissociation probability is larger. This process becomes faster when the strength of the dissociating field increases. That explains the observation that the effect of FRET is strongest at intermediate and high fields. The figure shows that the effect of FRET is stronger for model 3 than for model 2. That may be understood from the positive correlation of E_{exc} with $E_{\text{exc},b}$ within model 3, so that exciton relaxation in the Gaussian DOS does not necessarily reduce the sensitivity to a dissociating field. Within both models, a further increase of R_F , to values above 3.5 nm, is found to have no effect on the efficiency curves. Such a saturation effect is expected to occur when each exciton visits, before

dissociation or radiative decay due to fast diffusion, many molecules with a representative distribution of molecular environments. In principle, Dexter transfer can also contribute to the diffusion process. However, transfer rates for this process are not well known. Simulations for strong Dexter transfer for both models lead to a similar PL efficiency curve as obtained for strong FRET, with $R_F = 3.5$ nm or larger.

V. ACCURACY OF DEDUCING $E_{\text{exc},b}$ FROM FID EXPERIMENTS

A first estimate of the accuracy with which $E_{\text{exc},b}$ can be obtained from FID experiments may be deduced from the one-dimensional model without energetic disorder, without exciton diffusion, and with only nearest-neighbor hopping, that has been presented in Sec. II C. From Eq. (11), $E_{\text{exc},b}$ is, within that model, given by

$$E_{\text{exc},b} = |aeF_{1/2}| + \frac{e^2}{4\pi\epsilon_0\epsilon_r a} + k_B T \ln \left(\frac{\tau_{\text{rad}} \nu_1}{2} \right). \quad (16)$$

For the set of default parameters that has been assumed (see Table I), the potential energy difference $|aeF_{1/2}|$ between nearest-neighbor (NN) sites at the field $F_{1/2}$ is approximately 0.39 eV and the CT-state binding energy $E_{\text{CT},b}$ [the second term at the right-hand side in Eq. (16)] is approximately 0.48 eV. From Eq. (16), the sensitivity to the product $\tau_{\text{rad}} \nu_1$ is given by

$$(\Delta E_{\text{exc},b})_{\tau_{\text{rad}} \nu_1} = k_B T \ln(10) \Delta[\log_{10}(\tau_{\text{rad}} \nu_1)], \quad (17)$$

so that $E_{\text{exc},b}$ would be approximately 0.059 eV larger (at room temperature) than as obtained from Eq. (16) when the product $\tau_{\text{rad}} \nu_1$ would be a factor of 10 larger than as assumed. The sensitivity to ϵ_r is given by

$$(\Delta E_{\text{exc},b})_{\epsilon_r} = -E_{\text{CT},b} \frac{\Delta \epsilon_r}{\epsilon_r}, \quad (18)$$

so that Eq. (16) would yield a value of $E_{\text{exc},b}$ that is about 0.05 eV too large when ϵ_r would actually be 10% larger than as assumed. The sensitivity to a is given by

$$(\Delta E_{\text{exc},b})_a = [|aeF_{1/2}| - E_{\text{CT},b}] \frac{\Delta a}{a}, \quad (19)$$

so that Eq. (16) would yield a value of $E_{\text{exc},b}$ that is only about 0.009 eV too large when a would actually be 10% larger than as assumed. Due to partially compensating effects, the sensitivity to an error in a is thus expected to be very small.

The KMC simulation results that have been presented in Fig. 5 provide a more accurate view of the sensitivity $E_{\text{exc},b}$ to material parameters, as the simulations include the three-dimensional nature of the dissociation process and further complexities such as energetic disorder. When judging the sensitivity of the FID curves to parameter variations, we focus on the effects on $F_{1/2}$. Figure 5(a) shows that a change of $E_{\text{exc},b}$ by ± 0.1 eV would shift $F_{1/2}$ by $\Delta F_{1/2}^* \approx 0.08 \times 10^9$ V/m. When for a certain parameter x its uncertainty Δx leads to a shift of $F_{1/2}$ by a value $(\Delta F_{1/2})_x$, the resulting uncertainty of $E_{\text{exc},b}$ is $(\Delta E_{\text{exc},b})_x = 0.1 \times (\Delta F_{1/2})_x / \Delta F_{1/2}^*$ eV.

Table II gives, for each simulation parameter x , a conservative estimation of the experimental uncertainty Δx that we regard as realistic when a careful and dedicated effort is made

TABLE II. Overview of the estimated contributions of parameter value uncertainties $\pm \Delta x$ to the uncertainty $\pm (\Delta E_{\text{exc},b})_x$ of the value of $E_{\text{exc},b}$ that can be obtained from FID experiments, carried out for systems that are characterized by the set of simulation parameters that is given in Table I. The footnotes indicate how each parameter value can be determined.

Parameter x	Uncertainty Δx	$(\Delta E_{\text{exc},b})_x$ [eV]
$\log_{10}(\nu_1 [\text{s}^{-1}])^a$	0.5	0.035
$\sigma_{h,e}^a$	0.01–0.02 eV	0.020–0.040
ϵ_r^b	0.1–0.3	0.014–0.042
λ^c	0.1 nm	0.019
$\log_{10}(\tau_{\text{rad}} [\text{s}])^d$	0.2	0.014
a^e	0.05 nm	~0.01
σ_{exc}^f	0.02 eV	0.005
ρ_1 and ρ_2^g		j
p_{dip}^h		k
R_F^i		l

^aCharge-transport studies, neat films.

^bImpedance measurements.

^cCharge-transport studies, blended films.

^dTime-resolved PL measurements.

^eFilm volume density measurements.

^fPL emission spectrum measurements.

^gQuantum-chemical theory; see, e.g., paper II.

^hQuantum-chemical theory; see, e.g., Refs. [60] and [63].

ⁱMeasurement overlap optical absorption and emission spectra.

^jFigure 4(c) shows the sensitivity of $F_{1/2}$ to ρ_1 and ρ_2 .

^kFigure 5(b) shows the sensitivity of $F_{1/2}$ to p_{dip} .

^lFigure 5(f) shows the sensitivity of $F_{1/2}$ to R_F .

to obtain each parameter value from a thin-film study, using, for example, the methods that are indicated in the footnotes and taking realistic film-to-film variabilities into account. The last column gives the uncertainty $(\Delta E_{\text{exc},b})_x$ that follows from the simulations results in Sec. IV. The entries are given in the order of decreasing expected contribution to the uncertainty in $E_{\text{exc},b}$. Inspection of the results shows that the sensitivity to $\tau_{\text{rad}} \nu_1$, ϵ_r , and a is quite well described by Eqs. (17), (18), and (19), respectively.

The table shows that the overall accuracy of the value of $E_{\text{exc},b}$ that is deduced from FID experiments may be expected to be ~0.10–0.15 eV, under the conditions mentioned above and provided that uncertainties in the parameters for which no assessment has been given (ρ_1 , ρ_2 , p_{dip} , and R_F) do not contribute significantly. Important contributions to the uncertainty of $E_{\text{exc},b}$ are due to the uncertainties in ν_1 and $\sigma_{h,e}$. For hole transport, these quantities can be accurately determined from charge-transport studies, as has been recently confirmed by a comparison with quantum-chemical theory [65]. For electron transport, the presence of unavoidable extrinsic trap states in materials with a high LUMO energy [66] tends to complicate the analysis. The wave-function decay length can be determined from transport studies for host-guest systems [67]. Its uncertainty is correlated with an uncertainty in ν_1 and $\sigma_{h,e}$. Another important contribution to the uncertainty of $E_{\text{exc},b}$ is due to the uncertainty in ϵ_r . Space-charge-free reverse bias low-frequency capacitance measurements for single-layer sandwich-type devices with a sufficiently large

built-in voltage can provide ε_r with an accuracy that is better than 2% (see paper III). However, values of ε_r that are for the same material reported in the literature often show a much larger variability [63], which is not yet understood. The effective exciton lifetime τ_{eff} can be determined from time-resolved PL experiments with an accuracy that is better than a few percent. However, in the presence of quenching sites, exciton diffusion can lead to a value of τ_{eff} that is much smaller than τ_{rad} . In paper III, such an effect is reported for films of both isomers of MADN and is there included in the analysis. As such a complicating effect could occur more generally, Table II gives, for τ_{rad} , an effective uncertainty of 50%.

In addition to the systematic methodology for estimating the accuracy of deducing $E_{\text{exc},b}$ from FID experiments that has been discussed above, one could carry out further experiments that probe the consistency of the analysis method. In paper III, the consistency is judged from the results of photocurrent experiments. When the decrease of the PL intensity with increasing field is described as a result of full dissociation of electron-hole states, as we have done here, one expects that the normalized sums of the photocurrent and PL intensities are field independent. For the materials studied, the normalized total yield is indeed found to be field independent within 10% or better. We suggest in paper III that the small deviation could be due to nonradiative decay of field-induced charge-transfer excitons. Second, the consistency could be judged from the results of temperature-dependent experiments. The analysis that has been given in the present paper [Eqs. (16), (17)] indicates that the effect is sensitive to the product $\tau_{\text{rad}} \nu_1$. However, Eq. (17) suggests that the effect is expected to be relatively small: for the default parameters that are given in Table I, the effect of a temperature decrease from 300 to 200 K is expected to be similar to that of changing the binding energy at room temperature by about 0.05 eV. Much larger effects are expected by diluting the material systematically with a high-gap semiconductor material (leading to an increase of the $|F_{1/2}|$ field), or by blending systematically with a material with a more shallow HOMO energy or a deeper LUMO energy (leading to easier dissociation, and hence to a decrease of $|F_{1/2}|$). We are presently pursuing these various options for experimentally investigating the accuracy of the approach. The results are expected to provide a basis for judging the importance of refining the theoretical model.

Future refinements of the theoretical model should, first, include the photophysical processes of the field-induced charge-transfer states, such as radiative and nonradiative decay and spin-flip processes. As discussed above, paper III presents indications from photocurrent experiments that such effects can play a role. We note that the electron-hole interaction and radiative decay rate of field-induced CT states are expected to be smaller than that for exciplex states that can form spontaneously (in the absence of a field) after optical absorption in a blend of a donor and an acceptor molecule (see, e.g., Refs. [68] and [69]). Second, it would be of interest to carry out the KMC simulations for a thin-film structure that is more realistic. Such simulations would require using

molecular dynamics methods that provide a thin-film morphology, such as presented in Ref. [13] and paper II for the two isomers of MADN, combined with off-lattice KMC simulations that utilize *ab initio* calculated values of intermolecular transfer integrals. For mobility calculations, the feasibility of such an approach has been demonstrated (see, e.g., Refs. [70] and [14]). Model calculations suggest that the temperature and charge carrier density dependence of the mobility are not fundamentally affected by morphology effects [71]. The electric field dependence could be more strongly affected, although this has been studied so far only for a spatially random distribution of molecular sites instead of a distribution that is more consistent with actually measured radial distribution functions [72]. It is not *a priori* clear to what extent FID curves of neat film materials would be sensitive to details of the morphology. As a first step towards gaining more understanding of this sensitivity, we have calculated FID curves using 3D-KMC simulations for a face-centered-cubic (fcc) lattice, instead of a simple-cubic (sc) lattice, and for a sc lattice with a log-normal distribution of intermolecular transfer integrals. These simulations show that for the conditions considered, the main effect is a small broadening of the $\eta_{\text{PL}}(F)$ curves (see Sec. S1 of the Supplemental Material [73]). Material-specific simulations that are based on a proper description of the local three-dimensional positional and orientational disorder and of the resulting energy levels and intermolecular transfer integrals should be used to establish a more general picture.

VI. SUMMARY AND CONCLUSIONS

We have used 3D-KMC simulations to analyze the feasibility of deducing the singlet exciton binding energy in disordered small-molecule organic semiconductors from field-induced exciton dissociation experiments. The lattice model that is employed in the simulations has allowed the study of the sensitivity to various realistic experimental uncertainties. A sensitivity study for a material with an average exciton binding energy of $E_{\text{exc},b} = 1$ eV, and for a representative set of other material parameters (see Table I), suggests that obtaining $E_{\text{exc},b}$ with an accuracy of 0.1–0.15 eV should be feasible (see Table II). Attaining such an accuracy requires that the effects of static dipole moments on the energetic disorder and FRET or Dexter-type exciton diffusion are included in the analysis. The lattice model that has been employed neglects positional and orientational disorder and the resulting distributions of the intermolecular distances and charge-transfer rates. Quantum-chemical simulations will be needed to judge the relevance of these refinements. In paper II, such simulations are performed for the α and β isomers of MADN.

DATA AVAILABILITY

The data that support the findings of this article are openly available [74].

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