

## Towards a Unified Macroscopic Description of Exciton Diffusion in Organic Semiconductors

Jingrun Chen<sup>1,\*</sup>, Jason D. A. Lin<sup>2</sup> and Thuc-Quyen Nguyen<sup>2</sup>

<sup>1</sup> *Mathematical Center for Interdisciplinary Research and School of Mathematical Sciences, Soochow University, Suzhou, China;*

*Mathematics Department, University of California, Santa Barbara, CA93106, USA.*

<sup>2</sup> *Center for Polymers and Organic Solids, Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA.*

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**Abstract.** We study the exciton diffusion in organic semiconductors from a macroscopic viewpoint. In a unified way, we conduct the equivalence analysis between Monte-Carlo method and diffusion equation model for photoluminescence quenching and photocurrent spectrum measurements, in both the presence and the absence of Förster energy transfer effect. Connections of these two models to Stern-Volmer method and exciton-exciton annihilation method are also specified for the photoluminescence quenching measurement.

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### 1 Introduction

Over the past few decades, much attention has been focused on organic semiconductors for applications in various opto-electronic devices (see, *e.g.*, [15, 19, 23]). These materials are carbon-based compounds, and typically contain other elements such as N, O, H, S, and P. Organic semiconductors can be classified into three categories with increasing complexity [3, 15], including small molecules, oligomers, and polymers with atomic mass units ranging from several hundreds to at least several thousands.

From a microscopic perspective, exciton, a bound electron-hole pair, is the elementary excitation in opto-electronic devices such as light-emitting diodes (LEDs) and organic solar cells. The characteristic distance that an exciton travels during its lifetime  $\tau_0$  in a

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\*Corresponding author. *Email addresses:* jingrunchen@suda.edu.cn (J. Chen), nilnosaj5891@gmail.com (J. Lin), quyen@chem.ucsb.edu (T.-Q. Nguyen)

given material is defined as the exciton diffusion length  $L_D$ . Excitons can transport energy without carrying net electric charge, and thus plays a vital role in the function of these devices. A large  $L_D$  in organic LEDs may limit luminous efficiency if excitons diffuse to non-radiative quenching sites [1]. Conversely, a small  $L_D$  in organic photovoltaics (OPVs) limits the dissociation of excitons into free charges [12, 25].

Generally, there are two types of experimental methods to measure exciton diffusion length: Photoluminescence quenching measurement and photocurrent spectrum measurement. The former includes steady-state and time-resolved photoluminescence surface quenching, time-resolved photoluminescence bulk quenching, and exciton-exciton annihilation (*e.g.*, [11]). The latter includes solar cell photocurrent spectrum (*e.g.*, [17]). At the electronic level, physical processes behind experiments include exciton generation, exciton diffusion, exciton dissociation, exciton recombination, exciton-exciton annihilation, and exciton-environment interaction. Accordingly, various models are proposed to characterize exciton diffusion length, depending on how much information at the microscopic level is included. From a modeling viewpoint, these models can be grouped into either differential equation based or stochastic process based. Understanding the relationship between different models is not only complicated by the use of different mathematical descriptions but also the variety of organic materials and complexity of the underlying physical processes.

In this work, we show the equivalence between Monte-Carlo method for time-resolved photoluminescence bulk quenching, and diffusion equation models for both steady-state and time-resolved photoluminescence surface quenching in Sections 2.1-2.4. In addition, we make a connection between time-resolved photoluminescence bulk quenching with Monte-Carlo method and time-resolved photoluminescence bulk quenching with Stern-Volmer method under some experimentally controllable condition in Section 2.5. Moreover, we show in Section 2.6 that exciton-exciton annihilation method always tends to overestimate the exciton diffusion length compared with other models. For photocurrent spectrum measurement, we also show the equivalence between diffusion equation model and Monte-Carlo method in Section 3. Conclusion will be drawn in Section 4.

## 2 Photoluminescence quenching measurement

Consider prototypical film structures for photoluminescence quenching measurement in Fig. 1. For surface quenching measurement, a bi-layer is prepared of an organic semiconductor (donor) and an exciton quenching layer; see Fig. 1(b). For bulk quenching measurement, a blended film of the donor and quenchers is prepared; see Fig. 1(c). A single layer of the organic semiconductor is used to measure the intrinsic life time  $\tau_0$  of exciton in the donor; see Fig. 1(a). A monochromatic light is used to excite electrons in the donor layer. Excitons diffuse in the same layer and interact with the local environment after their generation. Eventually, an exciton either emits a photon and returns to its ground state or dissociates into a free electron and a free hole. As a result, the