Multiscale modeling of organic materials

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[334] `https://github.com/marrink-lab/vermouth-martinize`.

Summary

The field of organic electronics promises a host of thin, lightweight, flexible, and environmentally friendly electronic devices—such as solar cells, biosensors, and transistors. Such devices are made possible by the use of *organic materials*, materials constituted by organic molecules—that is, carbon-based molecules—which possibly possess interesting electronic properties. To fulfill this promise, scientists need to resolve one fundamental complication which finds its roots in the virtually infinite possibilities offered by organic molecules: master the relations between the molecular structure of the single molecules, their aggregate morphology—that is, how the molecules organize themselves to constitute the organic material—and the performance of the resulting electronic device. The formidable task of mastering these relations requires help from computational modeling. Once mastered and available at the fingertips of scientists via computational protocols, the experimental efforts currently necessary would be drastically reduced, and required only for a few lead compounds which passed successfully all the computational design steps. This would drastically accelerate the development of organic electronic devices, bringing the promise of organic electronics much closer to reality.

In this context, the aim of this thesis is to demonstrate how information on the molecular organization of organic materials can be obtained by a *multiscale modeling* approach. The term "multiscale" designates the combined use of various modeling techniques with the aim of covering a large range of length and time scales, from the molecular-scale towards the device-scale. To this end, the modeling techniques used in this thesis range from coarse-grain molecular dynamics simulations, used to address processes which occur on the larger length and time scales, to density functional theory calculations, used to address processes which occur on much shorter length and time scales. Coarse-grain models treat the system in a more approximate way by describing groups of atoms as effective interaction sites which interact following classical mechanics; models based on density functional theory treat instead even electrons explicitly, and thus must follow the more complex laws of quantum mechanics. The use of a wide range of computational techniques allows to connect features of the single molecules to their collective structural organization, and to understand how this in turn affects the electronic properties of the organic material, and thus of the resulting electronic device.

The quest for relations between the molecular structure of the single molecules, their aggregate morphology, and the performance of the resulting electronic device starts from improving the modeling of the *morphology*. None of the existing modeling techniques offered the combination of being able to 1) reach relevant length scales, 2) retain chemical specificity, 3) mimic experimental fabrication conditions such as solution-processing, and 4) be used in high-throughput studies. Chapter 2 presents a method which fulfills these requirements. The method has two key ingredients: *i)* the use of molecular dynamics simulations based on the Martini coarse-grain model, which can reach relevant length scales while retaining a sizable degree of chemical detail; the model is moreover suitable for high-throughput studies due to its modularity; *ii)* the use of computational protocols which take into account fabrication conditions of an organic thin film such as solution-processing. The method is not only applicable to organic materials for solar cells, as showcased in chapter 2, but also for any other organic electronic device, as shown in chapter 3 for organic thermoelectric blends. In both cases, the obtained simulated morphologies are in agreement with experimental findings, but also provide a molecular view on the structure of the materials and their evolution during fabrication processes.

The second paramount benefit of the method developed in chapter 2 is the possibility of easily converting, via backmapping techniques, the coarse-grained morphology to full atomistic resolution. This paves the way for advanced electronic structure calculations, for which atomistic details is required, in realistic morphologies of organic materials. This is shown in chapter 4, where the detailed structural conformations at the donor-acceptor interfaces of organic solar cells are resolved and studied as a function of processing conditions and molecular features. Moreover, the atomistic resolutions allows for the computation of energy levels relevant for the functioning of the solar cells. The findings of this chapter show that the use of organic molecules functionalized with polar side chains introduces energetic disorder, with potentially detrimental effects on the voltage of the resulting solar cells.

So far, the state-of-the-art Martini coarse-grain model has proven reliable enough to probe the larger length and time scales. Some limitations of this model are however described in detail in chapter 5. The key finding of the chapter is the importance of the density of particles present in the simulation. This critical parameter of the system can be greatly affected by bond lengths in the models; an inattentive use of bond length parameters can thus cause deviations from the parametrized behavior of the force field. In the view of these findings, the chapter discusses implications for the use of the current Martini force field, and suggests directions for reparametrization, effectively forming the basis of the next generation of the Martini force field.

The realization of the limitations concerning the Martini model described in chapter 5 initiated the development of a new major version of the force field, dubbed *Martini 3.0*. The key characteristic of the new Martini model is a much-improved balance between the interactions of the particles of different sizes which can be used to describe molecules. In chapter 6, the new parametrization, along with features and performances of the new Martini 3.0 models, is described focusing on small cyclic molecules, molecules which are, for example, particularly relevant for organic materials. Cyclic molecules constituted the main reference for the parameters of the newly recalibrated smaller particle sizes of the force field. This work is expected to boost and open new avenues in the use of the Martini model for systems containing such molecular fragments, such as organic materials relevant for electronics.

This thesis enables multiple developments and extensions, including the possibility of simulating an ever larger number of organic materials, while systematically connecting the obtained morphologies to the electronic properties which are fundamental to the functioning of the resulting electronic devices. Taken together, the findings of this thesis contribute to the route towards an age where the design of organic materials is based on computational models and simulations.

Samenvatting

Het vakgebied van de organische elektronica belooft de ontwikkeling van een grote verscheidenheid aan dunne, lichtgewicht, flexibele en milieuvriendelijke elektronische apparaten – zoals zonnecellen, biosensoren en transistoren – dankzij het gebruik van *organische materialen*. Zulke materialen bestaan uit organische moleculen – moleculen gebaseerd op koolstof – die mogelijk interessante elektronische eigenschappen bezitten. Om deze ontwikkeling mogelijk te maken moeten wetenschappers echter eerst een fundamenteel probleem oplossen waarvan de oorzaak ligt in het vrijwel oneindig aantal mogelijkheden die organische moleculen bieden: het begrijpen van de relatie tussen de moleculaire structuur van het individuele molecuul, zijn geaggregeerde morfologie – dat is hoe de moleculen zich organiseren tot het organische materiaal – en de prestaties van het van uit materiaal gefabriceerde apparaat. Computermodellen zijn nodig om deze enorme uitdaging aan te gaan. Wanneer men de relatie tussen molecuul, aggregaat en apparaat begrijpt en deze in de vorm van computationele protocollen beschikbaar zijn voor wetenschappers, zal de tijd die op dit moment nodig is voor experimenteel onderzoek drastisch omlaag gaan, en zullen experimentele testen alleen nodig zijn voor die materialen die succesvol alle computationele ontwerpstappen hebben doorlopen. Dit zou een drastische versnelling betekenen voor de ontwikkeling van organische elektronica, en een flinke stap in het realiseren van de belofte van organische elektronica.

In deze context is het doel van dit proefschrift te laten zien hoe informatie van de moleculaire organisatie van organische materialen kan worden verkregen via *multischaal modelleren*. De term “multischaal” duidt op het gecombineerde gebruik van verscheidene modelleertechnieken met het doel om een breed scala aan lengte- en tijdschalen te beschrijven, van de molecuulschaal tot aan de apparaatschaal. Voor dit doel worden er in dit proefschrift gebruik gemaakt van modelleertechnieken variërend van grofkorrelige moleculaire dynamica simulaties, die gebruikt worden om processen die op de grotere ruimte- en tijdschalen plaats vinden te omschrijven, tot aan dichtheidsfunctionaaltheorie, een modelleertechniek die processen beschrijft die op veel kortere tijd- en lengteschalen plaatsvinden. Grofkorrelige modellen schetsen moleculaire systemen meer bij benadering waarbij het groepen van atomen beschrijft als deeltjes die op elkaar inwerken volgens de wetten van de klassieke mechanica; dichtheidsfunctionaaltheorie beschrijft daarentegen zelfs elektronen expliciet en vereist daarom het gebruik van de complexere wetten van de kwantummechanica. Het gebruik van een groot scala aan computationele

technieken maakt het mogelijk om kenmerken van het individuele molecuul te verbinden met de structurele organisatie van het collectief en hoe dit op zijn beurt de elektronische eigenschappen van het organische materiaal en het resulterende apparaat beïnvloedt.

Het onderzoek naar de relatie tussen de structuur van het individuele molecuul, de morfologie van het aggregaat en de prestaties van het resulterende apparaat begint bij het verbeteren van het modeleren van de *morfologie*. Geen van de bestaande modelleertechnieken kon zowel 1) relevante lengteschalen behalen, 2) chemische specificiteit behouden, 3) experimentele fabricatie-omstandigheden nabootsen zoals oplossingsverwerking en 4) en gebruikt worden in zogeheten "high throughput" studies. Hoofdstuk 2 presenteert een methode die aan al deze voorwaarden voldoet. Deze methode heeft twee essentiële componenten: *i)* het gebruik van moleculaire dynamica simulaties gebaseerd op het grofkorrelige Martini model, dat relevante lengteschalen behaalt terwijl het een redelijk deel van de chemische details behoudt; het model is daarbij dankzij zijn modulariteit geschik voor "high-throughput" studies; *ii)* het gebruik van computerprotocollen die rekening houden met fabricagecondities van een organische film zoals oplossingsverwerking. De methode is niet alleen van toepassing op organische materialen voor zonnecellen, zoals uiteengezet in hoofdstuk 2, maar ook voor elk ander organisch elektronisch apparaat, zoals in hoofdstuk 3 gedemonstreerd wordt voor organische thermo-elektrische mengsels. In beide gevallen zijn de verkregen gesimuleerde morfologieën niet alleen in overeenstemming met experimentele bevindingen, maar bieden ook een beeld van de moleculaire structuur van de materialen en hun evolutie tijdens de fabricageprocessen.

Het tweede belangrijke voordeel van de in hoofdstuk 2 ontwikkelde methode is de mogelijkheid dat de grofkorrelige morfologie eenvoudig naar volledige atomistische resolutie te converteren is door gebruik te maken van de kennis over de correspondentie tussen de posities van de grofstoffelijke deeltjes en de atomen waaruit ze zijn opgebouwd. Dit maakt de weg vrij voor het doen van geavanceerde berekeningen van de elektronische structuur in realistische morfologieën van organische materialen, waarvoor volledig atomistisch detail nodig is. Dit wordt gedemonstreerd in hoofdstuk 4, waar de gedetailleerde structurele conformaties op het donor-acceptor raakvlak in zonnecellen worden ontrafeld en bestudeerd als functie van de fabricagecondities en moleculaire eigenschappen. Bovendien maakt de atomistische resolutie het mogelijk om energieniveaus te berekenen die relevant zijn voor het functioneren van de zonnecellen. De bevindingen van dit hoofdstuk laten zien dat het gebruik van organische moleculen die gefunctionaliseerd zijn met polaire zijketens onregelmatigheden in de energieniveaus veroorzaakt, met mogelijk schadelijke effecten op het voltage van de resulterende zonnecellen.

Het geavanceerde grofkorrelige Martini model bleek tot nu toe betrouwbaar genoeg voor het modelleren van de grotere lengte- en tijdschalen. Enkele beperkingen van dit model worden echter in hoofdstuk 5 in detail beschreven. De belangrijkste bevinding van het hoofdstuk is het belang van de dichtheid van de deeltjes in de simulatie. Deze kritieke parameter kan sterk worden beïnvloed door de bindingslengtes in de modellen; een onoplettend gebruik van verkorte bindingslengten kan resulteren in afwijkingen van het in het krachtenveld geparameteriseerde gedrag. Naar aanleiding van deze bevindingen worden in het hoofdstuk de implicaties voor het huidige Martini krachtenveld bediscussieerd en worden er aanbevelingen gedaan voor her-parameterisatie, daarbij de basis vormend voor de volgende generatie van het Martini krachtenveld.

De bewustwording over de in hoofdstuk 5 beschreven beperkingen van het Martini model initieerde de ontwikkeling van een nieuwe, belangrijke, versie van het krachtenveld, *Martini 3.0*. Een belangrijke eigenschap van het nieuwe Martini model is een sterk verbeterde balans van de wisselwerking tussen deeltjes van verschillende grootte die gebruikt kunnen worden om moleculen te beschrijven. In hoofdstuk 6 wordt de nieuwe parameterisatie beschreven samen met de kenmerken en de prestaties van de nieuwe Martini 3.0 modellen. Hierbij wordt vooral aandacht gegeven aan kleine cyclische moleculen die in het bijzonder belangrijk zijn voor organische materialen. De parameters van de nieuwe geherkalibreerde kleinere deeltjes in het krachtenveld worden voornamelijk gebruikt in cyclische moleculen. Verwacht wordt dat dit werk een boost geeft aan en nieuwe wegen zal openen voor het gebruik van het Martini model voor systemen met dergelijke moleculaire fragmenten, zoals organische materialen relevant voor elektronica.

Dit proefschrift maakt verscheidene ontwikkelingen en uitbreidingen mogelijk, waaronder de mogelijkheid tot het simuleren van een almaar groeiend aantal organische materialen, waarbij de verkregen morfologieën verbonden worden met de elektronische eigenschappen die fundamenteel zijn voor het functioneren van de resulterende elektronica. Bij elkaar genomen dragen de bevindingen in dit proefschrift bij aan de weg naar een tijdperk waarin het ontwerp van organische materialen is gebaseerd op computermodellen en simulaties.

Riepilogo

Il campo dell'elettronica organica promette lo sviluppo di un'ampia varietà di dispositivi elettronici – come per esempio celle solari, biosensori, o transistor – che in futuro saranno sottili, leggeri, flessibili, ecologici, e stampabili con tecniche come la stampa a getto d'inchiostro. Tali dispositivi sono ottenibili grazie all'uso di *materiali organici*, ovvero materiali composti da molecole organiche – vale a dire, molecole a base di carbonio – le quali possono godere di interessanti proprietà elettroniche. Per tenere fede a questa promessa, la scienza deve andare alla radice di un problema complesso che trova origine nelle infinite configurazioni adottabili dalle molecole organiche: scoprire le relazioni fondamentali che connettono la struttura delle singole molecole, l'organizzazione di un insieme di tali molecole, che costituiranno poi il materiale principale del dispositivo elettronico, e le caratteristiche del dispositivo stesso. Questa impresa necessita del supporto della modellazione computazionale. Una volta che queste relazioni fondamentali saranno modellate in software alla portata di scienziati e ingegneri, gli sforzi sperimentali attualmente richiesti saranno ridotti drasticamente ed applicati solo alle molecole organiche che supereranno con successo tutte le fasi di design computazionale. Ciò accelererebbe in maniera significativa lo sviluppo di dispositivi elettronici organici, spingendone l'introduzione nella realtà quotidiana.

L'obiettivo di questa tesi è quello di dimostrare l'efficacia di uno specifico approccio di *modellazione multiscala* per l'ottenimento di informazioni a livello molecolare sull'organizzazione di materiali organici. Il termine "multiscala" indica l'uso combinato di varie tecniche di modellazione computazionale al fine di coprire un ampio raggio di scale temporali e metriche, da quelle del dispositivo elettronico, a quelle della singola molecola. A tal fine, le tecniche utilizzate in questa tesi spaziano da simulazioni di dinamica molecolare di livello "coarse-grain", utilizzate per le scale temporali e metriche più ampie, fino a tecniche basate sulla teoria del funzionale della densità elettronica, utilizzate per le scale più ridotte. Modelli di tipo coarse-grain descrivono il sistema in modo più approssimato, inglobando gruppi di atomi in particelle (pseudo-atomi) che interagiscono seguendo leggi della meccanica classica, mentre modelli basati sulla teoria del funzionale della densità elettronica, trattando in modo esplicito particelle subatomiche come gli elettroni, devono essere fedeli alle complesse leggi della meccanica quantistica. L'impiego di diverse tecniche computazionali permette la connessione tra le caratteristiche delle singole

molecole e la loro organizzazione collettiva, associando di conseguenza le caratteristiche collettive alle proprietà elettroniche del materiale organico, e quindi del dispositivo finale.

La ricerca di relazioni fondamentali che connettano la struttura della singola molecola alle caratteristiche del risultante dispositivo elettronico, inizia con il miglioramento delle tecniche di simulazione della *morfologia* dei materiali organici, vale a dire, l'organizzazione collettiva delle molecole che vanno a costitutire il materiale. Nessuna delle tecniche di modellazione esistenti offre simultaneamente la possibilità di 1) raggiungere scale temporali e metriche adeguate, 2) mantenere un grado sufficiente di discriminazione tra molecole in base alla loro natura chimica, 3) simulare i processi sperimentali per la fabbricazione di dispositivi elettronici organici, come la stampa a getto d'inchiostro, 4) essere integrate in processi di design ad alta efficienza ("high-throughput"). Il secondo capitolo di questa tesi introduce un metodo in grado di soddisfare tali requisiti, il quale si basa sue due componenti fondamentali: *i)* l'utilizzo del modello coarse-grain Martini, che riesce a catturare efficientemente la chimica dei sistemi, e può essere utilizzato in schemi ad alta efficienza grazie alla sua modularità; *ii)* l'utilizzo di protocolli computazionali mirati a riprodurre i processi di fabbricazione usati in laboratorio. Nello stesso capitolo, il metodo viene inizialmente validato su una tipica cella fotovoltaica organica, con l'intento poi, di estenderne l'applicazione su qualsiasi dispositivo elettronico organico. Questo viene dimostrato concretamente nel terzo capitolo, dove lo stesso metodo viene applicato su dispositivi termoelettrici organici. In entrambi i casi, le morfologie dei materiali organici simulati sono in accordo con i dati sperimentali corrispondenti, fornendo in aggiunta una visione a livello molecolare della struttura dei materiali e della loro evoluzione durante i processi di fabbricazione.

Un altro beneficio derivante dal metodo sviluppato nel secondo capitolo, è la possibilità di convertire facilmente la morfologia dal livello coarse-grain, al livello atomistico, tramite cosiddette tecniche di "backmapping", le quali fanno uso della corrispondenza esistente fra gli pseudo-atomi coarse-grain e gli atomi che rappresentano. Tali metodi permettono così di calcolare proprietà elettroniche basate su morfologie che rappresentano più da vicino l'organizzazione reale dei materiali organici. Il quarto capitolo mostra come sfruttare questi metodi andando a studiare la struttura all'interfaccia tra i due componenti necessari al funzionamento di tipiche celle fotovoltaiche organiche. Tale struttura determina il principale funzionamento di queste celle, e nel capitolo, è riportato come essa possa essere studiata nel dettaglio e in funzione dei loro processi di fabbricazione. Inoltre, il dettaglio atomistico permette di predire proprietà elettroniche importanti per il funzionamento delle celle fotovoltaiche organiche. Nello specifico, i risultati del quarto capitolo indicano che l'uso di molecole organiche con catene laterali molto polari introduce disordine energetico, con potenziali effetti negativi sul voltaggio prodotto dalle celle solari.

Fino a questo punto, le simulazioni su scale temporali e metriche più ampie sono state basate sul modello coarse-grain Martini. Alcune limitazioni di questo modello vengono studiate dettagliatamente nel quinto capitolo, le cui conclusioni si focalizzano sull'importanza della densità delle particelle che vengono simulate, e come questa può essere influenzata drammaticamente dalle distanze di legame intramolecolari. Un uso distratto di tali distanze può portare a deviazioni dal corretto funzionamento del modello Martini. Sulla base di questi risultati, vengono chiarite delle linee guida per il corretto uso del modello; inoltre, il capitolo ne suggerisce spunti per il miglioramento, formando la base per una nuova versione del modello stesso.

La comprensione delle limitazioni del modello coarse-grain Martini, descritte nel quinto capitolo, ne hanno dato il via allo sviluppo di una nuova versione del, denominata *Martini 3.0*. La caratteristica chiave del nuovo modello è un miglior bilanciamento fra le particelle di diverse dimensioni utilizzate nelle simulazioni. Il sesto capitolo discute la nuova parametrizzazione, le caratteristiche, e l'efficienza di Martini 3.0 concentrandosi su molecole organiche cicliche, le quali sono particolarmente rilevanti nella simulazione di materiali organici, facilitando l'applicazione del metodo in questi sistemi.

In conclusione, questa tesi suggerisce molteplici sviluppi ed estensioni, compresa la possibilità di simulare un numero sempre maggiore di molecole organiche, e di connettere la morfologia del materiale organico alle proprietà elettroniche fondamentali per il funzionamento del dispositivo risultante. Nel loro insieme, i risultati di questa tesi contribuiscono a creare le fondamenta di un'era dove il design di dispositivi elettronici organici viene guidato da modelli computazionali e simulazioni.

List of Publications

- R. Alessandri, J. J. Uusitalo, A. H. de Vries, R. W. A. Havenith, S. J. Marrink, *Bulk Heterojunction Morphologies with Atomistic Resolution from Coarse-Grain Solvent Evaporation Simulations*, J. Am. Chem. Soc. **2017**, *139*, 3697–3705.

- L. Qiu[†], J. Liu[†], R. Alessandri, X. Qiu, M. Koopmans, R. W. A. Havenith, S. J. Marrink, R. C. Chiechi, L. J. A. Koster, J. C. Hummelen, *Enhancing Doping Efficiency by Improving Host-Dopant Miscibility for Fullerene-Based n-Type Thermoelectrics*, J. Mater. Chem. A **2017**, *5*, 21234–21241.

- J. Liu[†], L. Qiu[†], R. Alessandri, X. Qiu, G. Portale, J. Dong, W. Talsma, G. Ye, A. A. Sengrian, P. C. T. Souza, M. A. Loi, R. C. Chiechi, S. J. Marrink, J. C. Hummelen, L. J. A. Koster, *Enhancing Molecular n-Type Doping of Donor-Acceptor Copolymers by Tailoring Side Chains*, Adv. Mater. **2018**, 1704630.

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- S. Sami, P. A. B. Haase, R. Alessandri, R. Broer, R. W. A. Havenith, *Can the Dielectric Constant of Fullerene Derivatives Be Enhanced by Side Chain Manipulation? A Predictive First Principles Computational Study*, J. Phys. Chem. A **2018**, *122*, 3919–3926.

- R. Alessandri[†], P. C. T. Souza[†], S. Thallmair, M. N. Melo, A. H. de Vries, S. J. Marrink, *Pitfalls of the Martini Model*, J. Chem. Theory Comput. **2019**, DOI: 10.1021/acs.jctc.9b00473.

- P. C. T. Souza[†], S. Thallmair[†], P. Conflitti, J. C. Ramírez Palacios, R. Alessandri, S. Raniolo, V. Limongelli, S. J. Marrink, *Protein-Ligand Binding with the Coarse-Grained Martini Model*, submitted (**2019**).

- S. Sami, R. Alessandri, R. Broer, R. W. A. Havenith, *Molecular Origin and Frequency Dependent Response of High Dielectric Constant Organic Semiconductors*, submitted (**2019**).

- A. S. Bondarenko, I. Patmanidis, R. Alessandri, P. C. T. Souza, A. H. de Vries, S. J. Marrink, T. L. C. Jansen, J. Knoester, *Multiscale Modeling of Structural and Optical Properties of Complex Supramolecular Aggregates*, submitted (**2019**).

- R. Alessandri, S. Sami, J. Barnoud, A. H. de Vries, S. J. Marrink, R. W. A. Havenith, *Polar Side Chain-Induced Disorder of Charge Carrier Energy Levels of Organic Semiconductors*, in preparation (**2019**).

[†]Equal contribution.

- P. C. T. Souza, R. Alessandri, *et al.*, *Martini 3.0: a General Purpose Force Field for Coarse-Grain Molecular Dynamics*, in preparation (**2019**; open-beta version available at cgmartini.nl).
- R. Alessandri, J. Barnoud, I. Patmanidis, A. H. de Vries, P. C. T. Souza, S. J. Marrink, *Martini 3.0 Coarse-Grained Force Field: Ring Structures*, in preparation (**2019**).

Associated data and code available online at:

- http://cgmartini.nl
  - P3HT, PCBM, and chlorobenzene Martini 2.2 force field files
  - PTEG-1, PP, N-DBMI, and TEG-DMBI Martini 2.2 force field files
- https://figshare.com/authors/Riccardo_Alessandri/4043948
  - P3HT, PCBM, and chlorobenzene GROMOS 53A6 atomistic force field files
  - PTEG-1, PP, and N-DBMI GROMOS 53A6 atomistic force field files
- https://github.com/ricalessandri/
  - script to run solvent evaporation simulations
  - script to compute scattering curves
  - script to “polymerize” atomistic P3HT

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Riccardo