Photophysics of nanomaterials for opto-electronic applications

Simon Kahmann

November 8, 2017

University of Groningen
Friedrich-Alexander Universität Erlangen-Nürnberg
Contents

1 Introduction 1

2 Materials 4

2.1 Nanoscale Semiconductors 4

2.2 Organic Semiconductors 5

2.2.1 Conjugated Polymers 5

2.2.2 Interaction with Light 10

2.2.3 Excited States in Organic Solids 12

2.2.4 Carrier Transport in Disordered Systems 17

2.2.5 Charge Generation 20

2.3 Carbon Nanotubes 22

2.3.1 Opto-electronic properties 22

2.3.2 Single Walled Carbon Nanotube Spectroscopy 27

2.3.3 Sorting and Selecting Carbon Nanotubes 29

2.4 Colloidal Quantum Dots 31

2.4.1 Physical Properties 31

2.4.2 Lead Sulphide Colloidal Quantum Dots 32

2.4.3 Colloidal Quantum Dot Solids 33

2.4.4 Surface Chemistry 36

3 Experimental Techniques for Optical Spectroscopy 53

3.1 FTIR spectroscopy 53

3.1.1 Measurement Principle and Advantages 54

3.1.2 Fourier Transformation 55

3.2 Photoluminescence Spectroscopy 56

3.2.1 Principle 56

3.2.2 Ultrafast Techniques 57

3.3 Photoinduced Absorption Spectroscopy 58

3.3.1 Basic Principle 58

3.3.2 Steady State Photoinduced Absorption Spectroscopy 60

3.3.3 Transient Absorption Spectroscopy 61
## CONTENTS

4 Monitoring Polaron in Narrow Band Gap Polymers 64
  4.1 Introduction ........................................... 64
  4.2 Results and Discussion ............................... 65
  4.3 Conclusion ........................................... 71
  4.4 Methods ................................................ 73

5 Working Mechanism of Ternary Organic Solar Cells 77
  5.1 Introduction ........................................... 77
  5.2 Results and Discussion ............................... 78
  5.3 Conclusion ........................................... 85
  5.4 Methods ................................................ 86

6 Hybrid Excited States in Polymer Wrapped CNTs 89
  6.1 Introduction ........................................... 89
  6.2 Results and Discussion ............................... 90
  6.3 Conclusion ........................................... 97
  6.4 Methods ................................................ 99

7 Charge Transfer between Polymers and CQDs 104
  7.1 Introduction ........................................... 104
  7.2 Results and Discussion ............................... 105
  7.3 Conclusion ........................................... 111
  7.4 Methods ................................................ 112

8 Trap States in Lead Sulphide Colloidal Quantum Dots 115
  8.1 Introduction ........................................... 115
  8.2 Results and Discussion ............................... 116
  8.3 Conclusion ........................................... 123
  8.4 Methods ................................................ 124

Summary and Outlook 127

Sammenvatting 130

Appendix 132

Symbols and Abbreviations 141

List of Publications 147

Acknowledgements 148
List of Figures

2.1 Semiconductor density of states with respect to dimensionality .................................. 5
2.2 Hybridisation of atomic orbitals in carbon ................................................................... 6
2.3 Molecular orbitals and their energy levels ...................................................................... 7
2.4 Overview of different semiconducting polymers ............................................................. 8
2.5 Energy levels of donor-acceptor polymers .................................................................... 9
2.6 Jablonski scheme .......................................................................................................... 10
2.7 Frank-Condon principle and vibronic side peaks ............................................................ 11
2.8 Wannier-Mott and Frenkel excitons in semiconductors .................................................. 12
2.9 Polaron stabilisation mechanisms .................................................................................. 13
2.10 Polaron energy levels and optically allowed transitions .................................................. 15
2.11 Energy levels in different states of condensed matter .................................................... 16
2.12 Mechanisms for exciton migration ............................................................................... 18
2.13 Exciton motion through a Gaussian distribution of states .............................................. 18
2.14 Charge transfer state formation and dissociation ............................................................ 21
2.15 CNT chirality indices and lattice vectors from graphene ................................................. 23
2.16 Construction of the CNT band dispersion .................................................................... 24
2.17 DOS and band gap of metallic and semiconducting CNTs .............................................. 25
2.18 Optically allowed and forbidden transitions in CNTs ..................................................... 25
2.19 Excited many body states reported for CNTs ............................................................... 26
2.20 Absorption- and 2D-PL spectrum of CNTs ................................................................. 28
2.21 Energy gap for PbS CQDs with respect to their size ....................................................... 32
2.22 Impact of disorder and coupling on the transport in CQD solids ................................. 35
2.23 Surface chemistry of PbS CQDs .................................................................................. 38

3.1 Main components of a Michelson interferometer ............................................................ 54
3.2 Explanation of the Fourier transformation ..................................................................... 56
3.3 Illustration of the transient PL set-up ........................................................................... 58
3.4 Measurement principle and signals in PIA spectroscopy ................................................. 59
3.5 Steady state set-ups for PIA spectroscopy ..................................................................... 61
3.6 Transient absorption spectroscopy set-up ..................................................................... 62

4.1 Optically allowed transitions for differently charged polymers ...................................... 65
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>Absorbance and PIA spectra of C-/Si-PCPDTBT</td>
</tr>
<tr>
<td>4.3</td>
<td>Calculated absorption spectra for C-/Si-PCPDTBT oligomers</td>
</tr>
<tr>
<td>4.4</td>
<td>Electron-hole density of a PCPDTBT oligomer and aggregate</td>
</tr>
<tr>
<td>4.5</td>
<td>Explanation of polymer IRAVs in the MIR spectral region</td>
</tr>
<tr>
<td>4.6</td>
<td>Different excitation PIA spectra of neat polymers</td>
</tr>
<tr>
<td>5.1</td>
<td>Materials and solar cell characterisation for the ternary device</td>
</tr>
<tr>
<td>5.2</td>
<td>PL spectra of neat and blended organic films</td>
</tr>
<tr>
<td>5.3</td>
<td>PL spectra for polymer blends of different concentration</td>
</tr>
<tr>
<td>5.4</td>
<td>Steady state PIA spectra of the organic blends</td>
</tr>
<tr>
<td>6.1</td>
<td>Energy levels and absorption spectra of polymer wrapped CNTs</td>
</tr>
<tr>
<td>6.2</td>
<td>Photoluminescence spectra of polymer wrapped CNTs</td>
</tr>
<tr>
<td>6.3</td>
<td>NIR PIA and TA of polymer wrapped CNTs</td>
</tr>
<tr>
<td>6.4</td>
<td>MIR PIA of polymer wrapped CNTs</td>
</tr>
<tr>
<td>6.5</td>
<td>Calculated first excitation for a polymer wrapped CNT</td>
</tr>
<tr>
<td>6.6</td>
<td>Representative molecular orbitals for P3DDT wrapped CNTs</td>
</tr>
<tr>
<td>7.1</td>
<td>Energy levels and absorption spectra of PbS CQDs and PCPDTBT</td>
</tr>
<tr>
<td>7.2</td>
<td>PL spectra of neat and blended films of PCPDTBT and PbS CQDs</td>
</tr>
<tr>
<td>7.3</td>
<td>TA and EQE of neat and blended films of PCPDTBT and PbS</td>
</tr>
<tr>
<td>7.4</td>
<td>J-V curves of fabricated solar cells and AFM images of their ALs</td>
</tr>
<tr>
<td>8.1</td>
<td>Sketch and TEM images of employed ligands and CQDs</td>
</tr>
<tr>
<td>8.2</td>
<td>Absorbance spectra of CQDs in solution and as a film</td>
</tr>
<tr>
<td>8.3</td>
<td>PIA spectra of PbS CQDs with different size and ligands</td>
</tr>
<tr>
<td>8.4</td>
<td>PL upon ligand variation and TEM image of degraded CQDs</td>
</tr>
<tr>
<td>8.5</td>
<td>Data for degraded or differently washed PbS_OA</td>
</tr>
<tr>
<td>8.6</td>
<td>Vibrational spectra and Fano calculations for PbS CQDs</td>
</tr>
<tr>
<td>A1</td>
<td>Additional electrical characterisation of organic solar cells</td>
</tr>
<tr>
<td>A2</td>
<td>PL spectra of PDCBT:PC_{70}BM</td>
</tr>
<tr>
<td>A3</td>
<td>Absorption spectra of PF12-related samples</td>
</tr>
<tr>
<td>A4</td>
<td>MIR PIA spectra of neat P3DDT</td>
</tr>
<tr>
<td>A5</td>
<td>PIA spectra of a P3DDT:PCBM blend with different energy</td>
</tr>
<tr>
<td>A6</td>
<td>PIA spectra of P3DDT wrapped CNTs</td>
</tr>
<tr>
<td>A7</td>
<td>PIA spectra of P3DDT wrapped CNTs with excess polymer</td>
</tr>
<tr>
<td>A8</td>
<td>PIA spectra of neat PF12 upon above and below gap excitation</td>
</tr>
<tr>
<td>A9</td>
<td>PIA spectra of a PF12:PCBM blend</td>
</tr>
<tr>
<td>A10</td>
<td>PIA spectra of PF12 wrapped CNTs</td>
</tr>
</tbody>
</table>
List of Tables

2.1 Exciton Bohr radii of relevant semiconductors ............................................. 33

5.1 Electrical parameters of organic solar cells ................................................. 79
5.2 Extracted PL lifetimes for organic films ....................................................... 81
5.3 Extracted PL lifetimes for polymer blends ................................................... 84

7.1 PL lifetimes of hybrid blends ........................................................................ 108

A1 Calculated transition energies for PCPDTBT aggregates ................................. 132
A2 Calculated transition energies for trions in CNTs .......................................... 137
A3 Composition of excited states for P3DDT wrapped CNTs ................................. 137
A4 Peak positions and widths of PIA bands of PbS QDs ....................................... 138
A5 Molecular vibrations associated with oleic acid ............................................ 138
A6 Molecular vibrations associated with 1,4-benzenedithiol ............................... 139