Contents

Preface *xiii*

1 Introduction of Organic Thermoelectrics *1*
Yingqiao Ma, Ye Zou, Chong-an Di, and Daoben Zhu
1.1 Brief Introduction and Historical Overview *1*
1.2 Thermoelectric Effect *4*
1.2.1 Seebeck Effect *4*
1.2.2 Peltier Effect *6*
1.2.3 Thomson Effect *6*
1.2.4 Other Related Effects *7*
1.3 Thermoelectric Parameters *9*
1.3.1 Basic Parameters *9*
1.3.2 Power Conversion Efficiency and TE Figure-of-Merit *10*
1.3.2.1 Power Conversion Efficiency *10*
1.3.2.2 Thermoelectric Figure-of-Merit and Power Factor *12*
1.4 Challenges and Perspectives *13*
References *16*

2 Theoretical Model and Progress of Organic Thermoelectric Materials *19*
Fengjiao Zhang and Jia Zhu
2.1 Introduction *19*
2.2 Charge Transport *20*
2.2.1 Basic Charge Transport Model *22*
2.2.1.1 Band and Band-like Transport *23*
2.2.1.2 Hopping Transport *25*
2.2.2 Boltzmann Transport Theory *26*
2.2.3 Trade-off Relationship Between σ and S *29*
2.3 Thermal Transport *32*
2.3.1 Electronic Thermal Conductivity *33*
2.3.2 Lattice Thermal Conductivity *33*

2.4 Theoretical Progress in OTE Materials *37*
2.4.1 TE Conversion in Small Molecules *38*
2.4.2 TE Conversion in Polymer *40*
2.5 Conclusion *44*
References *45*

3 P-Type Organic Thermoelectric Materials *49*
Dongyang Wang, Xiao Zhang, Liyao Liu, Yimeng Sun, and Chong-an Di
3.1 Introduction *49*
3.2 Charge Transfer Complexes *52*
3.3 Conventional Conducting Polymers *52*
3.3.1 Polyaniline *53*
3.3.2 Polypyrrole *55*
3.3.3 Polycarbazole Derivatives *55*
3.3.4 PEDOT-Based Materials *56*
3.3.5 Metal–Organic Coordination Polymers *68*
3.4 Doped High Mobility Semiconductors *69*
3.4.1 Polythiophene-Based Materials *69*
3.4.1.1 Polythiophene *69*
3.4.1.2 PBTTT *69*
3.4.1.3 P3HT *71*
3.4.2 Indacenodithiophene Derivatives *73*
3.4.3 Diketopyrrolopyrrole Derivatives *73*
3.4.4 Pentacene *75*
3.4.5 Metal Phthalocyanines *77*
3.4.6 Strategies for Performance Optimization *78*
3.5 Perspective *80*
References *82*

4 N-Type Organic Thermoelectric Materials *87*
Yimeng Sun and Liyao Liu
4.1 Introduction *87*
4.2 Materials and Properties *88*
4.2.1 Metal–Organic Coordination Polymers *88*
4.2.2 Conjugated Polymers *90*
4.2.3 Organic Small Molecules *97*
4.3 Strategies for the Performance Optimization *105*
4.3.1 Molecular Design *105*
4.3.1.1 Molecular Backbones *105*
4.3.1.2 Side Chains *107*
4.3.2 Dopant *110*
4.4 Summary and Perspective *116*
References *117*

5 Hybrid/Composite Organic Thermoelectric Materials *123*
Xiaoying Ma, Danfeng Zhi, Ziling Jiang, Zihan He, Yimeng Sun, and Fengjiao Zhang
5.1 Introduction *123*
5.2 Fundamental Effect and Theory *124*
5.2.1 Percolation Theory *125*
5.2.2 Interface Effects *126*
5.2.3 Energy Filter Effects *126*
5.3 Materials and Properties *128*
5.3.1 Organic–Inorganic Hybrid Materials *128*
5.3.1.1 Te *131*
5.3.1.2 Ge *133*
5.3.1.3 Bi_2Te_3 *134*
5.3.1.4 Other Inorganic Fillers *137*
5.3.2 Polymer-Carbon Material Composites *138*
5.3.2.1 Carbon Nanotubes (CNTs) *138*
5.3.2.2 Graphene (GP) and C60 *141*
5.3.3 Organic–Organic TE Blends *144*
5.3.4 Organic Coordination Based Compounds *145*
5.4 Strategies of Hybrid/Composite OTE Materials Fabrication and Optimization *147*
5.4.1 Optimizing the Fabrication Techniques *147*
5.4.2 Controlling the Multidimensional Structure of the Fillers *151*
5.4.3 Modification of Organic Matrix *152*
5.5 Conclusion and Perspective *155*
References *156*

6 Organic Ionic Thermoelectric Materials and Devices *161*
Yuanrong Bao, Dekai Ye, and Fei Jiao
6.1 Introduction *161*
6.2 Fundamentals of Ionic Thermoelectrics *162*
6.2.1 Soret Effect *162*
6.2.2 Energy Conversion Mechanisms for Ionic Thermoelectric Materials *163*
6.2.2.1 Ionic Thermoelectric Supercapacitors *163*
6.2.2.2 Thermogalvanic Cells *164*
6.2.3 Ionic Conductivity *165*
6.2.4 Ionic Seebeck Coefficient *167*
6.2.5 Ionic Thermal Conductivity *169*
6.3 Organic i-TE Materials Based on Electrolytes *169*
6.3.1 Liquid Materials *170*
6.3.1.1 Solutions *170*
6.3.1.2 Ionic Liquids *171*

6.3.2 Solid and Quasi-Solid Materials *172*
6.4 Organic i-TE Materials Based on Mixed Conductors *177*
6.5 Organic i-TE Devices and Applications *178*
6.5.1 Thermal-charged Supercapacitors *180*
6.5.2 Heat-gated Transistors *183*
6.5.3 Sensors *184*
6.5.4 Generators *185*
6.6 Differences Between Ionic and Electronic Thermoelectrics *187*
6.7 Perspectives and Challenges *188*
References *189*

7 Engineered Doping of Organic Thermoelectric Materials *195*
Jiamin Ding, Lanyi Xiang, Zheng Ji, Liyao Liu, Ye Zou, and Chong-an Di
7.1 Introduction *195*
7.2 Chemical Doping *197*
7.2.1 Doping Mechanism *197*
7.2.1.1 Charge Transfer Doping *198*
7.2.1.2 Acid–Base Doping *200*
7.2.2 Dopant *201*
7.2.2.1 p-Type Dopants *202*
7.2.2.2 n-Type Dopants *204*
7.2.3 Doping Method *205*
7.2.3.1 Solution-Based Process *205*
7.2.3.2 Thermal Evaporation *208*
7.3 Electrochemical Doping *210*
7.4 Electric-Field Induced Interfacial Doping *212*
7.5 Photodoping *216*
7.6 Doping Strategies for OTE Materials *219*
7.6.1 Precise Manipulation of Carrier Concentration and Mobility *219*
7.6.2 Tailoring DOS *221*
7.6.3 Building Low-Dimensional Materials *221*
7.6.4 Improving Stability *223*
7.6.5 Doping OSCs Without Dopants *224*
7.6.6 Achieving Homogeneous Doping *226*
7.7 Conclusions and Perspectives *227*
References *229*

8 Organic Thermoelectric Devices *237*
Yue Zhao, Ziling Jiang, Wei Wang, Danfeng Zhi, Fengjiao Zhang, and Chong-an Di
8.1 Introduction *237*
8.1.1 Device Geometry *238*
8.1.2 Performance Parameter *240*

8.1.2.1 Power Output *240*
8.1.2.2 Cooling Capacity and Heat Flux Density *241*
8.1.2.3 Efficiency *242*
8.1.3 Process Techniques *242*
8.2 Power Generator *245*
8.2.1 Flexible Device *248*
8.2.2 Fabric Device *250*
8.2.3 Stretchable and Self-Healed Device *255*
8.3 Peltier Cooler *258*
8.4 Multifunctional Applications *261*
8.4.1 Temperature Sensor *261*
8.4.2 Photodetector *263*
8.4.3 Multifunctional Sensor *266*
8.5 Conclusion *269*
References *270*

9 Single-Molecule Thermoelectric Devices *275*
Kai Song, Junfeng Lin, Yingqiao Ma, Xuwei Song, and Yaping Zang
9.1 Introduction *275*
9.2 Fundamental Background and Experimental Techniques *276*
9.2.1 Fundamental Background *276*
9.2.1.1 Electrical Conductivity *276*
9.2.1.2 Seebeck Coefficient *277*
9.2.1.3 Thermal Conductivity *278*
9.2.1.4 ZT Value *279*
9.2.1.5 Theoretical Predictions of Single-Molecule Thermoelectric Performance *279*
9.2.2 Experimental Techniques *281*
9.2.2.1 Scanning Tunneling Microscope-Break Junction (STM-BJ) *282*
9.2.2.2 Mechanically Controlled Break Junction (MCBJ) *283*
9.2.2.3 Atomic Force Microscope (AFM) *286*
9.2.2.4 Liquid Metal Electrode *288*
9.2.2.5 Three Terminal Devices *290*
9.2.2.6 Scanning Tunneling Seebeck Microscopy (STSM) *290*
9.3 Advances in Single-Molecule Thermoelectric Devices *296*
9.3.1 Seebeck Coefficient Measurements *296*
9.3.1.1 Seebeck Coefficient of Atomic Metallic Contacts *296*
9.3.1.2 Length Dependence *297*
9.3.1.3 Anchor Groups *301*
9.3.1.4 Substituent Effects *302*
9.3.1.5 Electrode Materials *303*
9.3.1.6 Metal Dopants *304*
9.3.1.7 Quantum Interference Effects *306*

9.3.1.8 Electrostatic Control *307*
9.3.2 Thermal Conductance Measurements *309*
9.3.3 Peltier Effect Measurements *311*
9.4 Perspectives *312*
References *313*

10 Measurement Techniques of Thermoelectric-related Performance *319*
Jiamin Ding, Zhiyi Li, Fengjiao Zhang, Ye Zou, and Chong-an Di
10.1 Introduction *319*
10.2 Measurement of Electrical Conductivity *319*
10.2.1 Basic Principle of Four-Probe Method *320*
10.2.2 Determination of Resistivity *321*
10.2.2.1 Parallel Electrode Structure *321*
10.2.2.2 Van der Pauw Structure *322*
10.3 Measurement of Seebeck Coefficient *324*
10.3.1 Temperature Difference Creation *324*
10.3.2 Temperature Difference Measurement *324*
10.3.2.1 Thermocouple *325*
10.3.2.2 Thermal Resistance *326*
10.3.2.3 Infrared Method *326*
10.3.3 Seebeck Voltage Measurement *327*
10.3.3.1 Static Method *328*
10.3.3.2 Quasi-Static Method *328*
10.3.4 Error Analysis *328*
10.4 Measurement of Thermal Conductivity *330*
10.4.1 Thermal Conductivity of Bulk Materials *331*
10.4.1.1 Absolute and Comparative Techniques *331*
10.4.1.2 Pulsed Power Technique *332*
10.4.1.3 Transient Plane Source Method *333*
10.4.2 Thermal Conductivity of Thin-Film Materials *334*
10.4.2.1 3ω Method *334*
10.4.2.2 Transient Thermoreflectance Technique *340*
10.4.2.3 Laser Flash Method *342*
10.5 Simultaneous Measurement of Key Parameters *343*
10.5.1 Measurement Chip *343*
10.5.2 Measurement of Key TE Parameters *344*
10.6 Determination of Carrier Concentration *346*
10.6.1 Field-Effect Transistor *347*
10.6.2 Hall Effect *348*
10.7 Determination of Electronic Structure *351*
10.7.1 Photoelectron Spectroscopy *351*
10.7.1.1 Ultraviolet and X-Ray Photoelectron Spectroscopy *351*
10.7.1.2 Inverse Photoelectron Spectroscopy *355*
10.7.1.3 Photoelectron Yield Spectroscopy *356*

10.7.2 Optical Spectroscopy *357*
10.7.3 Kelvin Probe Force Microscopy *358*
10.7.4 Scanning Tunneling Spectroscopy *358*
10.7.5 Cycle Voltammetry *359*
10.8 Summary *359*
References *360*

Index *367*