

Contents

List of Contributors	v
Foreword	vii
Preface	ix

I Functionalized TTFs

1 Synthetic Approaches to Unsymmetrical, Dimeric and Oligomeric TTFs	3
1.1 Introduction	3
1.2 Synthesis of Functionalized Unsymmetrical TTFs <i>via</i> Condensation of Two 1,3-Dichalcogenole Rings	3
1.2.1 Nonselective Strategy: Cross-coupling Reactions	3
A. Method A: Cross-coupling Reaction of 1,3-Dithiolium Salts	4
B. Method B: Cross-coupling Reaction of 1,3-Dichalcogenole-2-chalcogenones	5
1.2.2 Recent Applications of Method B: Synthesis of Functionalized Unsymmetrical TTFs, TSFs and Bis-fused TTF-type Donors	8
A. Synthesis of TTF-CO ₂ Me (Type I)	8
B. Synthesis of Types I–III	9
1.2.3 Selective Strategies: Wittig- and Wittig-Horner-type Condensations and Organometallic Route	10
A. Method C: Wittig-type Condensation	11
B. Method D: Wittig-Horner-type Condensation	13
C. Method E: Yamada Coupling Reaction	16
1.3 Synthesis of Functionalized Unsymmetrical TTFs <i>via</i> Substitution on the TTF Core and Its Periphery	18
1.3.1 Conversion of Functional Groups	18
A. Conversion TTF-CO ₂ R → TTF-CH ₂ OH and TTF-CONR ₂	19
B. Conversion TTF-CHO → TTF-CH ₂ NR ₂	20
C. Conversion into TTF-X (X = halogen), TTF-C ₆₀ and TTF-SnR ₃	20
1.3.2 Synthesis of Bis- and Bi-TTFs	22
1.3.3 Synthesis of TTF Chalcogenides	24
1.3.4 Conversion of Protected TTF Chalcogenolates into Other Functionalized TTFs	25
1.3.5 Conversion of Protected TTF Chalcogenolates into Dimeric and Oligomeric TTFs	26
1.4 Summary	30
References	30

2	Tetrachalcogenafulvalenes with Four Additional Heteroatoms	35
2.1	Introduction	35
2.2	Preparation of Building Blocks	37
2.3	Synthesis of TCFs	42
2.4	Electrochemical Behavior of TCFs	46
2.5	Role of Additional Functional Groups in the Synthesis and Properties of TCFs	48
2.6	Formation and Properties of RCs and Other Charged Species	51
2.7	Design of New Materials	53
2.8	Summary	55
	References	55
3	Halogenated TTFs	59
3.1	Introduction	59
3.2	Synthesis and Properties of Halogenated TTFs	59
3.2.1	Chlorination and Bromination	60
3.2.2	Iodinated TTFs	62
3.2.3	DSDTFs and TSeFs	65
3.3	Electrochemical Properties of Halogenated TTFs	67
3.4	Crystal Structure and Physical Properties of Charge Transfer Salts	68
3.4.1	Charge Transfer Salts of Chloro- and Bromo-TTFs	69
3.4.2	Iodine Bond: A Special Case of the Halogen Bond	69
3.4.3	Cation Radical Salts of IEDT	70
3.4.4	Donor-acceptor Complexes of Iodinated TTFs	71
3.4.5	Donor-anion Network in DIETS Salts	73
3.4.6	FeCl ₄ and FeBr ₄ Salts of DIETS and DIETSe	75
3.4.7	Metallic and Ferromagnetic Salts (DIEDO) ₂ [M(mnt) ₂] (M = Ni, Pt)	75
3.4.8	Hexagonal System of DIPS Salts	77
3.4.9	Superconductivity of θ -(DIETS) ₂ [Au(CN) ₄] under the Uniaxial Strain	78
3.5	Summary and Outlook	80
	References	81
4	Oxygen Analogues of TTFs	83
4.1	Introduction	83
4.2	Tetraoxafulvalene (TOF) and Related Compounds	85
4.3	BEDO-TTF and (MeO) ₄ TTF	87
4.3.1	Redox Properties and CT Complexes with Organic Acceptor Molecules	87
4.3.2	Self-assembling Nature of BO—I ₃ -type Packing Pattern	89
4.3.3	Other Packing Patterns of Conductive BO Complexes	93
4.3.4	Superconductors and Fermiology of BO Complexes	95
4.3.5	Fundamental Date of BO in the Complexes	99
4.3.6	Thin Films Composed of BO Complexes	101
4.3.7	Some Specific Complexes of BO	102
4.3.8	(MeO) ₄ TTF	103
4.4	DBTTFs Having Alkoxy Groups	103
4.5	EDO-TTF and Its Derivatives	106
4.6	Sulfur-selenium Analogues of EDO-TTF and Its Derivatives	111
4.7	Ethyleneoxythio-substituted TTFs	113

4.8 Summary and Outlook	114
References	114
5 Selenium Analogues of TTFs	119
5.1 Introduction	119
5.2 Synthesis of Selenocycle-fused TTFs	122
5.3 Titanocene Method: Synthesis of TSFs and STFs	123
5.4 Synthesis of STFs <i>via</i> Me ₃ Al-promoted Reaction	125
5.5 One-pot Synthesis of 1,3-Diselenole-2-selones	126
5.6 Outer Thio- and Seleno-cycle Formation <i>via</i> Transalkylation Reaction on Chalcogen Atom(s)	128
5.7 Synthesis of Heterocycle-fused TSFs <i>via</i> Protected TSF-thiolate and -selenolate Anions	130
5.8 Conducting Salts of New Selenium Analogues of TTFs	131
5.9 Summary and Outlook	133
References	134
6 TTFs with Organic Stable Radicals	137
6.1 Introduction	137
6.2 Organic Conductors Incorporating Inorganic Spins	138
6.3 Magnetic Conductors Composed of Dimeric Donors	139
6.3.1 Spin Alignment Based on Degenerated Molecular Orbitals	139
6.3.2 Ion-radical Salt of the Cross-cyclophane Type Twin Donor	139
6.4 Switchable Spin System Composed of Spin-polarized Donors	141
6.4.1 Spin-polarized Donors	141
6.4.2 Design of TTF-based Spin-polarized Donors	143
6.4.3 Spin-polarized Polyradical Donors	145
6.4.4 Preparation of TTF-based Tetraradical Donors	145
6.5 Assembled TTF Derivatives Carrying Stable Radicals	146
6.5.1 Nitroxide-based Donor Radicals	146
6.5.2 Ion-radical Salt of Spin-polarized Donors	147
6.6 Summary and Outlook	151
References	151
7 TTFs as Ligands of Metal Complexes	155
7.1 Introduction	155
7.2 Ni, Pd and Pt Complexes with TTFdithiolato Ligands	156
7.3 Cu Complexes with TTFdithiolato Ligands	163
7.4 CuBr ₂ Complexes with TTF Derivatives	165
7.5 Au Complexes with TTFdithiolato Ligands	166
7.6 Hg Complexes with TTFdithiolato Ligands	167
7.7 V Complexes with TTFdithiolato Ligands	169
7.8 Mn Complexes with TTFdithiolato Ligands	170
7.9 Neutral Metal Complex Oligomers with TTFdithiolato Groups	171
7.10 Summary and Outlook	171
References	172

II Dimeric TTFs

8	Bi- and Bis-TTFs	177
8.1	Introduction	177
8.2	Bi-TTF and Its Derivatives	178
8.2.1	Synthesis	178
8.2.2	Structures and Properties	183
8.2.3	Electric Conductivities and Crystal Structures	186
8.3	Conjugated Bis-TTFs Linked by π -Systems	191
8.3.1	Synthesis	191
8.3.2	Structures and Properties	196
8.4	Conjugated Bis-TTFs Linked by Heteroatoms	199
8.5	Summary and Outlook	201
	References	202
9	Cyclophane-type TTFs and TSFs	205
9.1	Introduction	205
9.2	Double-bridged TTF Phanes	206
9.3	Quadruple-bridged TTF Phanes of Parallel-stacked Type	213
9.4	Quadruple-bridged TTF Phanes of Crisscross-stacks Type	215
9.5	Triple-layered TTF Phanes	219
9.6	Double-bridged TSF Phanes	221
9.7	Summary and Outlook	225
	References	225
10	Bis-fused TTFs —Tetrathiapentalene Donors	227
10.1	Introduction	227
10.2	Synthesis and Properties of Bis-fused TTFs	228
10.3	Structures and Physical Properties of Bis-fused TTF Conductors	231
10.3.1	(BDT-TTP) A_x and (ST-TTP) $_2A$	231
10.3.2	κ -Type Salts Based on Bis-fused TTFs	235
10.3.3	TMEO-TTP and TMEO-ST-TTP Salts	236
10.3.4	Conducting Materials Based on TMET-TTP and Its Analogues	238
10.3.5	(BEDT-TTP) $_2I_3$ and (EP-TTP) $_2Au(CN)_2$	240
10.3.6	(CPTM-TTP) $_4A$ ($A = PF_6, AsF_6$ and SbF_6)	240
10.3.7	(TTM-TTP)(I_3) $_x$	241
10.4	Analogues of Bis-fused TTFs	242
10.5	Radical Cation Salts Based on DTEDT and DSEDS	246
10.6	Radical Cation Salts Based on (Thio)pyran Analogues	248
10.7	Tris-fused TTFs	251
10.8	Summary and Outlook	253
	References	254

III 1,3-Dithiol-2-ylidene Donors

11 Dihydro-TTFs and Bis-fused 1,3-Dithiol-2-ylidene Donors	261
11.1 Introduction	261
11.2 DHTTFs	262
11.2.1 Heterocycle-annulated DHTTFs and Their Seleno-analogues	263
11.2.2 Superconducting DODHT Salts	265
11.2.3 Miscellaneous DHTTF-containing Compounds	267
11.3 BDY Donors	269
11.3.1 Synthesis, Molecular Structures and Electrochemical Properties	270
11.3.2 CT Materials Based on BDH-TTP	272
11.3.3 Superconducting BDA-TTP Salts	275
11.3.4 Tetrachloroferrate (III) Salts of BDA-TTP	277
11.3.5 Other CT Materials Based on BDA-TTP	281
11.3.6 CT Materials Based on DHDA-TTP	282
11.4 Summary and Outlook	284
References	284
12 Bis(1,3-dithiol-2-ylidene) Donors with a Conjugated Spacer Group	287
12.1 Introduction	287
12.2 TTF Vinylogues	287
12.3 TTF Analogues Containing Aromatic Rings as Spacer	294
12.4 <i>p</i> -Quinodimethane Analogues of TTF	300
12.5 Summary and Outlook	308
References	308
13 Bis(1,3-dithiol-2-ylidene) Donors with a Heteroquinonoid-spacer Group	311
13.1 Introduction	311
13.2 Bis(1,3-dithiol-2-ylidene) Donors with a Thienoquinonoid- or Selenoquinonoid-spacer Group: BDTT and BDTS Type Donors	312
13.2.1 Synthesis	312
13.2.2 Oxidation Potentials	314
13.3 Bis(1,3-dithiol-2-ylidene) Donors with a Fused Heteroquinonoid-spacer Group: BDTBF, BDTBT and BDTBS Type Donors	315
13.3.1 Synthesis	316
13.3.2 Oxidation Potentials	317
13.3.3 TCNQ Complexes	318
13.3.4 Crystal Structures and Electrical Properties of (BEDT-BDTBT) ₃ (ReO ₄) ₂ , BEDT-BDTBF·BF ₄ and (BEDT-BDTBS) ₂ (X) ₃ (X = ClO ₄ , BF ₄ and ReO ₄)	318
13.3.5 Crystal Structures and Electrical Properties of (BEDT-BDTBF) ₂ X (X = PF ₆ and AsF ₆) and (BEDT-BDTBF) ₂ SbF ₆ (PhCl) _{0.5}	321
13.4 Bis(1,3-dithiol-2-ylidene) Donors with a 5,7-Dihydrofuro[3,4-b]pyrazine-5,7-diyldene-spacer Group	322
13.4.1 Synthesis, Physical Properties and Oxidation Potentials	323
13.4.2 Crystal Structures and Electrical Properties of (BDTFP) ₂ X(PhCl) (X = PF ₆ and AsF ₆)	323

13.5 Bis(4,5-ethylenedioxy-1,3-dithiol-2-ylidene) Donor with a Dihydrothienoquinonoid-spacer Group	326
13.5.1 Synthesis, Physical Properties and Oxidation Potentials of BO-HBDTT and BO-BDTT	327
13.5.2 Crystal Structures and Electrical Properties of BO-HBDTT Salts	327
13.6 Bis(4,5-ethylenedithio-1,3-diselenol-2-ylidene) Donor with a Dihydrothienoquinonoid-spacer Group	331
13.6.1 Synthesis and Oxidation Potentials	332
13.6.2 Crystal Structures and π -d Interactions in δ^- -(BEDT-HBDST) ₂ FeX ₄ (X = Cl and Br)	332
13.6.3 Electrical Properties of Tetrahedral and Octahedral Anion Salts of BEDT-HBDST	334
13.7 Summary and Outlook	335
References	336
14 Donor Systems with Multi-1,3-dithiol-2-ylidene Units	339
14.1 Introduction	339
14.2 TTFs with Multi-DT Units	339
14.3 TTF Vinylogues with Multi-DT Units	342
14.4 Trimethylenemethane and Tetramethylenethane Systems	346
14.5 [n]Radialenes (n = 4–6) with Multi-DT Units	351
14.6 [n]Dendralenes (n = 3, 4) with Multi-DT Units	357
14.7 Miscellaneous Donors Containing Multi-DT Units	361
14.8 Summary and Outlook	362
References	362

IV Applications of TTFs

15 Macrocyclic, Molecular and Supramolecular TTF Systems	367
15.1 Introduction	367
15.2 Key Properties of TTF	367
15.3 Applications of TTF Building Blocks	368
15.4 TTF Systems Based on TTF Tetrathiolate	369
15.4.1 TTF-macrocycles, -belts and -cages	369
15.4.2 TTF-based Ligands	372
15.5 An Orthogonal TTF Building Block	374
15.6 Pyrrolo-annulated TTFs	375
15.6.1 Synthesis	376
15.6.2 Electrochemistry	377
15.6.3 HOMO Orbitals	378
15.7 Applications of Pyrrolo-TTFs	379
15.7.1 Asymmetric Monopyrrolo-TTF Building Block	379
15.7.2 A Pyrrolo-TTF Belt	379
15.7.3 Tetrathiafulvaleno-annulated Porphyrins	380
15.8 Catenanes and Rotaxanes Incorporating TTF	382
15.8.1 Binding Studies between TTF Derivatives and CBPQT ⁴⁺	384
15.8.2 A Bistable [2]Rotaxane Incorporating a TTF Unit	387

15.9 Summary and Outlook	390
References 390	
16 TTF-acceptor Type Molecules 393	
16.1 Introduction	393
16.2 Nonconventional Applications of TTF	395
16.3 Polarized TTF Molecules	396
16.4 TTF- σ -acceptor Molecules: Molecular Rectification	399
16.5 TTF- σ -acceptor Molecules: Photovoltaic Applications	403
16.6 TTF- π -acceptor Molecules: Nonlinear Optical Applications	408
16.7 Noncovalent TTF-acceptor Interactions: Supramolecular Applications	412
16.8 Summary and Outlook	413
References 413	
17 TTF Polymers and Dendritic TTFs 417	
17.1 General Aspects and Background	417
17.2 Side-chain Polymers	417
17.3 Main-chain Polymers	420
17.4 Metal Coordination Polymers	423
17.5 Dendritic TTFs	425
17.6 Summary and Outlook	432
References 433	
Subject Index	435
Compound Index	441