

<b>ABSTRACT</b>	<b>III</b>
<b>TABLE OF CONTENTS</b>	<b>V</b>
<b>ABBREVIATIONS</b>	<b>XI</b>
<b>INTRODUCTION</b>	<b>1</b>
1. MOTIVATION AND AIM	2
2. GLOBAL ENERGY	5
2.1. Yesterday	5
2.2. Today	7
2.3. Tomorrow	9
3. RENEWABLE ENERGY	10
3.1. Water	11
3.2. Wind	12
3.3. Sun	13
4. PHOTOVOLTAIC TECHNOLOGIES	16
5. DYE-SENSITIZED SOLAR CELLS	18
<b>COPPER(I) DYE-SENSITIZED SOLAR CELLS</b>	<b>21</b>
6. COPPER – PHOTOPHYSICALLY ACTIVE, EARTH-ABUNDANT, CHEAP	22
7. DESIGN AND WORKING PRINCIPLE OF N-TYPE DYE-SENSITIZED SOLAR CELLS	25
7.1. Components	25
7.1.1. Working Electrode	25
7.1.2. Photosensitizer	29
7.1.3. Counter Electrode	36
7.1.4. Electrolyte	36
7.2. Working Principle	38
7.2.1. n-Type Dye-Sensitized Solar Cells	38
8. CHARACTERISATION	42
8.1. UV-Vis Spectroscopy	42
8.1.1. Instrumental Details	42
8.1.2. Solid-state UV-Vis Spectroscopy	43
8.2. Solar Simulator	44
8.2.1. Instrumental Details	44
8.2.2. <i>J-V</i> Measurements	46
8.3. External Quantum Efficiency	49
8.3.1. Instrumental Details	49
8.3.2. EQE Measurements	50

8.4. Electrical Impedance Spectroscopy	52
8.4.1. Instrumental Details	52
8.4.2. EIS Measurements	53
<b>SYNTHETIC STRATEGY AND CHARACTERIZATION</b>	<b>57</b>
9. TARGET MOLECULES	58
9.1. 2,2'-Bipyridine-Based Ligands	58
9.2. Heterocyclic N <sup>4</sup> NX Ancillary Ligands	61
10. SYNTHETIC STRATEGY	63
11. CHARACTERIZATION	67
11.1. NMR Spectroscopy	67
11.2. UV-Vis Spectroscopy	76
11.3. Mass Spectrometry	82
11.4. Electrochemistry	84
11.5. Crystal Structures	87
11.5.1. Crystal Structure Data	92
11.6. DFT calculations	93
<b>DEVICE FABRICATION</b>	<b>97</b>
12. EQUIPMENT DETAILS	98
13. GENERAL DEVICE FABRICATION	100
<b>FROM BPY TO N<sup>4</sup>NX</b>	<b>103</b>
14. 2,2'-BIPYRIDINE ANCILLARY LIGANDS	106
14.1. Prologue: Substituents and Halogens	107
14.2. Minimizing the Excess of Ancillary Ligand and the Total Process Time in the Dye-Assembly Process	113
14.3. Combination of the Best Performing Substituent and Halogen	123
14.4. Influence of the Co-adsorbent Cheno on the Efficiency	127
14.5. Regeneration of the Dye on the Semiconductor Surface	139
14.6. 2,2'-Bipyridine-Based Ligands with Different Functional Groups	143
15. N <sup>4</sup> NX ANCILLARY LIGANDS	147
15.1. A New Type of Ancillary Ligand for Copper(I)-Based Dye-Sensitized Solar Cells: N <sup>4</sup> NX	148
15.2. Outlook: Optimization of the N <sup>4</sup> NS Ligand	171

<b>PANCHROMATIC CO-SENSITIZED COPPER(I) DYE-SENSITIZED SOLAR CELLS</b>	<b>179</b>
16. CO-SENSITIZATION PRE-TESTS WITH A COPPER(I)-DYE AND N719	183
17. THE HISTORY OF "BLORANGE"	196
<b>EXPERIMENTAL PART</b>	<b>233</b>
18. GENERAL INSTRUMENTS AND METHODS	234
19. ANCILLARY LIGAND SYNTHESIS	235
19.1. 2,2'-Bipyridine-Based Ligands	235
19.1.1. 4,4'-Di-(4-bromophenyl)-6,6'-dimethyl-2,2'-bipyridine ( <b>L-Br</b> )	235
19.1.2. 4,4'-Di-(4-iodophenyl)-6,6'-dimethyl-2,2'-bipyridine ( <b>L-I</b> )	236
19.1.3. 4,4'-Di-(4-iodophenyl)-6,6'-diphenyl-2,2'-bipyridine ( <b><sup>Ph</sup>L-I</b> )	238
19.1.4. 4,4'-Di-(4-dimethylaminophenyl)-6,6'-diphenyl-2,2'-bipyridine ( <b>L-NMe<sub>2</sub></b> )	239
19.1.5. 4,4'-Di-(4-phenoxyphenyl)-6,6'-diphenyl-2,2'-bipyridine ( <b>L-OPh</b> )	240
19.1.6. 4,4'-Di-(4- <sup>i</sup> butylphenyl)-6,6'-diphenyl-2,2'-bipyridine ( <b>L-<i>t</i>-Bu</b> )	242
19.2. Heterocyclic N <sup>^</sup> NX Ancillary Ligands	244
19.2.1. 2-(6-Methylpyridin-2-yl)-1 <i>H</i> -benzo[ <i>d</i> ]imidazole (N <sup>^</sup> NNH)	244
19.2.2. 1-Methyl-2-(6-methylpyridin-2-yl)-1 <i>H</i> -benzo[ <i>d</i> ]imidazole (N <sup>^</sup> NNMe)	244
19.2.3. 2-(6-Methylpyridin-2-yl)benzo[ <i>d</i> ]oxazole (N <sup>^</sup> NO)	245
19.2.4. 2-(6-Methylpyridin-2-yl)benzo[ <i>d</i> ]thiazole (N <sup>^</sup> NS)	246
19.2.5. 2-(6-Phenylpyridin-2-yl)benzo[ <i>d</i> ]thiazole ( <b><sup>Ph</sup>N<sup>^</sup>NS</b> )	246
19.2.6. 2-(Quinolin-2-yl)benzo[ <i>d</i> ]thiazole ( <b><sup>Qu</sup>N<sup>^</sup>NS</b> )	247
19.2.7. 2-(6-(Difluoromethyl)pyridin-2-yl)benzo[ <i>d</i> ]thiazole ( <b><sup>CF</sup>F<sub>2</sub>N<sup>^</sup>NS</b> )	248
19.2.8. 2-(6-(Trifluoromethyl)pyridin-2-yl)benzo[ <i>d</i> ]thiazole ( <b><sup>CF</sup>F<sub>3</sub>N<sup>^</sup>NS</b> )	248
19.2.9. 2-(6-Methylpyridin-2-yl)-6-nitrobenzo[ <i>d</i> ]thiazole (N <sup>^</sup> NS(NO <sub>2</sub> ))	249
19.2.10. 2-(6-Methylpyridin-2-yl)benzo[ <i>d</i> ]thiazole-6-amine (N <sup>^</sup> NS(NH <sub>2</sub> ))	250
19.2.11. <i>N</i> -Methyl-2-(6-methylpyridin-2-yl)benzo[ <i>d</i> ]thiazole-6-amine (N <sup>^</sup> NS(NHMe))	251
19.2.12. <i>N,N</i> -Dimethyl-2-(6-methylpyridin-2-yl)benzo[ <i>d</i> ]thiazole-6-amine (N <sup>^</sup> NS(NMe <sub>2</sub> ))	252
20. COPPER(I) COMPLEX SYNTHESIS	254
20.1. 2,2'-Bipyridine-Ligand-Based Complexes	254
20.1.1. [Cu(L-I) <sub>2</sub> ][PF <sub>6</sub> ]	254
20.1.2. [Cu(L-NMe <sub>2</sub> ) <sub>2</sub> ][PF <sub>6</sub> ]	255
20.1.3. [Cu(L-OPh) <sub>2</sub> ][PF <sub>6</sub> ]	256
20.1.4. [Cu(L- <i>t</i> -Bu) <sub>2</sub> ][PF <sub>6</sub> ]	257
20.2. Heterocyclic N <sup>^</sup> NX Ancillary Ligands-Based Complexes	258
20.2.1. [Cu(N <sup>^</sup> NNH) <sub>2</sub> ][PF <sub>6</sub> ]	258
20.2.2. [Cu(N <sup>^</sup> NNMe) <sub>2</sub> ][PF <sub>6</sub> ]	259
20.2.3. [Cu(N <sup>^</sup> NO) <sub>2</sub> ][PF <sub>6</sub> ]	259
20.2.4. [Cu(N <sup>^</sup> NS) <sub>2</sub> ][PF <sub>6</sub> ]	260

20.2.5. [Cu( <b><sup>Ph</sup>N<sup>^</sup>NS</b> ) <sub>2</sub> ][PF <sub>6</sub> ]	261
20.2.6. [Cu( <b><sup>Qu</sup>N<sup>^</sup>NS</b> ) <sub>2</sub> ][PF <sub>6</sub> ]	262
20.2.7. [Cu( <b><sup>CF</sup>F<sub>2</sub>N<sup>^</sup>NS</b> ) <sub>2</sub> ][PF <sub>6</sub> ]	262
20.2.8. [Cu( <b><sup>CF</sup>F<sub>3</sub>N<sup>^</sup>NS</b> ) <sub>2</sub> ][PF <sub>6</sub> ]	263
20.2.9. [Cu(N <sup>^</sup> NS(NO <sub>2</sub> )) <sub>2</sub> ][PF <sub>6</sub> ]	264
20.2.10. [Cu(N <sup>^</sup> NS(NH <sub>2</sub> )) <sub>2</sub> ][PF <sub>6</sub> ]	265
20.2.11. [Cu(N <sup>^</sup> NS(NHMe)) <sub>2</sub> ][PF <sub>6</sub> ]	265
20.2.12. [Cu(N <sup>^</sup> NS(NMe <sub>2</sub> )) <sub>2</sub> ][PF <sub>6</sub> ]	266
21. ANCHORING LIGAND SYNTHESIS	267
21.1. ((6,6'-Dimethyl-[2,2'-bipyridine]-4,4'-diyl)-bis(4,1-phenylene))bis(phosphonic acid) ( <b>ALP1</b> )	267
21.2. ((6,6'-Diphenyl-[2,2'-bipyridine]-4,4'-diyl)-bis(4,1-phenylene))bis(phosphonic acid) ( <b><sup>Ph</sup>ALP1</b> )	269
<b>CONCLUSION &amp; OUTLOOK</b>	<b>271</b>
<b>ACKNOWLEDGEMENTS</b>	<b>275</b>
<b>REFERENCES</b>	<b>279</b>
<b>CURRICULUM VITAE</b>	<b>289</b>