Reducing interfacial recombination for photovoltage enhancement in mesoscopic solar cells

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NANYANG TECHNOLOGICAL UNIVERSITY

**REDUCING INTERFACIAL RECOMBINATION
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IN MESOSCOPIC SOLAR CELLS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Abstract

Mesoscopic solar cells, including dye-sensitized solar cells (DSCs), have been regarded as one of the promising low-cost energy conversion technologies for the next generation of solar cells. Inspired by natural photosynthesis, DSCs are built up from different components, handling light harvesting, charge transport and regeneration processes, in an appropriate energy level alignment. In traditional DSCs employing an I^-/I_3^- electrolyte, the loss in potential, particular in overpotential for regeneration, has become the key drawback, which limits its power conversion efficiency. The newly emerging Co(II/III) redox couples have reduced the loss in overpotential, however, significant interfacial recombination between electrons in the conduction band of the semiconductor (usually TiO_2) and electrolyte is a major concern in achieving an efficient device with a high photovoltage. This thesis focuses on reducing the interfacial recombination to achieve high photovoltages in liquid state DSCs through the modulation of electrolyte components, surface passivation and structural modification of cobalt-based redox mediators. In addition, the development of a new dopant for solid state perovskite solar cells is discussed.

The first study involves the modulation of photovoltage by 4-*tert*-butylpyridine (TBP), an electrolyte additive, which greatly enhances the recombination resistance. Its viscous nature, however, leads to a mass transport limitation in the Co redox system, which lowers the cell's photocurrent density, reconfirming the need for other additives in the Co(II/III) redox electrolyte. The second study involves the introduction of cyanobiphenyl derivatives as electrolyte additives in overcoming the mass transport limitation. An electrochemical impedance spectroscopy study revealed the interfacial recombination is greatly reduced, yielding higher photovoltage compared to the device with only TBP in electrolyte. The overall cell performance is enhanced with this additive and stable DSCs are achievable.

The inadequate protection of the TiO_2 surface by the electrolyte additive has led to the study on controlling the interfacial recombination by surface passivation. It has been ascertained that the use of alkanephosphonic acids assist in enhancing the recombination resistance and charge collection efficiency over a wide range of potentials. With the grafted TiO_2 photoanode, the blocking of the interaction between TiO_2 and electrolyte is significantly enhanced. The advantage of having bulky groups in disconnecting the contact between TiO_2 and electrolyte was implemented in the new cobalt-based redox shuttle, MY14. The presence of isopropyl groups in MY14 reduces the back reaction without any mass transport limitations, as confirmed by the photocurrent transient measurements.

Finally, in the solid state perovskite solar cell, the electrolyte was replaced by a solid state hole conductor (spiro-OMeTAD) which possesses more positive redox potential and results in higher photovoltage. The photovoltage is further improved through chemical doping of the hole conductor using the newly synthesized cobalt-based dopant, MY11. The conductivity of the hole conductor was increased by two orders of magnitude which guarantees better charge transport. MY11 exhibits deepest redox potential among all the current cobalt-based dopant and is important for doping a wide range of hole conducting materials for solution-processed photovoltaics.

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Table of Contents

Abstract.....	i
Acknowledgements.....	ii
Table of Contents.....	iv
List of Figures.....	vii
List of Tables.....	xiii
List of Abbreviations.....	xiv
Introduction	1
1.1 Background and motivation.....	1
1.2 Thesis objectives and scope.....	7
1.3 Thesis organization.....	9
1.4 Contribution of thesis	11
Literature Review	12
2.1 Dye-sensitized solar cells (DSCs) and its operating principle.....	12
2.2 Evaluation of power conversion efficiency	15
2.3 Redox electrolyte	18
2.3.1 Iodide/triiodide electrolyte	18
2.3.2 Limitation of iodide/triiodide redox system.....	19
2.3.3 Co(II/III) redox couples for DSCs	20
2.4 Surface passivation	27
2.5 Cobalt dopants for spiro-OMeTAD	30

2.6 Organometal halide perovskite solar cells	31
Experimental Section	34
3.1 Materials preparation	34
3.1.1 Synthesis of Co(II/III) redox mediators	34
3.1.2 Synthesis of dopant for spiro-OMeTAD.....	36
3.1.3 Synthesis of methylammonium iodide.....	39
3.2 Solar cell fabrication.....	39
3.2.1 Preparation of PEDOT counter electrodes.....	39
3.2.2 Fabrication of conventional DSCs and solid state perovskite solar cells	41
3.2.3 Composition of electrolytes	43
3.3 Characterization techniques.....	45
Modulating photovoltage in Co(II/III) mediated DSCs by electrolyte additive	49
4.1 Photovoltaic characteristics	50
4.2 Mass transport limitation	56
4.3 Reducing interfacial recombination.....	60
4.4 Summary.....	63
Controlling interfacial recombination <i>via</i> adsorption of cyanobiphenyl derivatives	65
5.1 Influences of additives on photovoltaics characteristics	66
5.2 Electrochemical impedance study on interfacial recombination	70
5.3 Mass transport and device stability.....	74
5.4 Summary.....	76

Enhancing recombination resistance and charge collection efficiency through surface passivation	78
6.1 Solvent-dependent passivation	79
6.2 Chain length effect in preventing back reaction	83
6.3 Influence of photosensitizers	87
6.2 Summary	90
Hindering electron recapture through structural modification of cobalt redox mediators	92
7.1 Design and synthesis of cobalt(II/III) redox mediator	93
7.2 Photovoltaic characteristics	94
7.3 Impedance and photocurrent transient study	97
7.4 Summary	100
Enhanced charge transfer of spiro-OMeTAD in perovskite solar cells	102
8.1 Design and synthesis of dopant	104
8.2 Charge transfer reaction between dopant and spiro-OMeTAD	106
8.3 Photovoltaic characteristics	110
8.4 Summary	113
Conclusions and future recommendations	114
9.1 Conclusions of thesis	114
9.2 Future outlook	117
Patent	120
Publications	120
References	123

List of Figures

Figure 1. Schematic energy level of typical DSCs. V_{OC} is determined by the difference Fermi level (E_F) of TiO_2 and the redox potential of the electrolyte. Overpotential is required for electron injection and dye regeneration.....	4
Figure 2. Maximum obtainable power conversion efficiencies versus absorption onset for various photovoltage losses. The model assumes an external quantum efficiency of 90% with the rise from the onset of absorption occurring over a range of 50 nm and a constant fill factor of 0.75 [16]......	5
Figure 3. Schematic structure of DSCs.	13
Figure 4. Simple energy level diagram with charge transfer processes occurring in DSCs under illumination.	14
Figure 5. Typical I-V and P-V curve of a photovoltaic device.	16
Figure 6. UV-Vis absorption spectra of TBAI, $TBAI_3$ and the iodine radical anion ($I_2^{\cdot-}$) in acetonitrile [14].	20
Figure 7. Outer-orbital diagram of high spin Co^{II} ion and low spin Co^{III} ion.....	21
Figure 8. UV-Vis absorption spectra of I/I_3^- , $[Co(bpy)_3]^{II/III}$ and N3 dye in mesoporous TiO_2 films [17].	21
Figure 9. (a) Photocurrent density vs. light intensity for different porosity. Transient photocurrent for porosity of (b) 0.52 and (c) 0.59. 1 sun corresponds to 100 mW cm^{-2} [59].	25
Figure 10. FESEM images of annealed TiO_2 NT electrodes with 11 μm thickness [60].	26
Figure 11. Cycling stability of symmetrical dummy cells with Pt-FTO (left) electrodes and GNP-FTO (G96) electrodes (right) in acetonitrile solution of $Co^{II/III}(bpy)_3$ [63].....	27
Figure 12. (a) IV characteristics of spiro-MeOTAD films spin-cast from $CHCl_3$ solution containing different amounts of FK102 dopant (b) Derived electrical conductivity as a function of doping level [82]......	31

Figure 13. Typical cubic perovskite structure bearing chemical formula of ABX_3 where A is cation, B is metal ion and X is anion.	32
Figure 14. Schematic diagrams of cross-sectional device of planar and mesoscopic devices.	33
Figure 15. (a) Chemical structure of PEDOT and (b) PEDOT-deposited flourine-doped tin oxide (FTO) glass substrates (c) Top view FESEM image of PEDOT counter electrode deposited on FTO.	40
Figure 16. Schematic diagram of dye sensitized solar cell with PEDOT counter electrode and Co-complex redox electrolyte.	41
Figure 17. Schematic diagram of perovskite formation and device architecture.	43
Figure 18.(a) EIS spectrum measured at V_{oc} and (b) complete equivalent circuit model for fitting [31].	46
Figure 19. (a) recombination resistance and (b) chemical capacitance of DSCs measured under different applied voltage [31].	47
Figure 20. Chemical structures of (a) cobalt ^{II/III} tris(bipyridyl) and (b) D35 photosensitizer.	50
Figure 21. (a) Photocurrent-voltage (I - V) characteristics under illumination with increasing TBP concentration in 0.1 M Co^{2+} electrolyte (light intensity: 100mWcm ⁻² , AM1.5G). (b) Short-circuit current and open-circuit voltage of DSCs with different TBP concentrations in 0.1 M Co^{2+} electrolyte.	52
Figure 22. Absorption spectra of D35 on TiO_2 film after treated with 0.1 M TBP and 0.5 M TBP electrolyte and the inset shows the picture of the photoanodes.	54
Figure 23. Short-circuit current (J_{sc}) and open-circuit voltage (V_{oc}) of DSCs with 0.4 M TBP concentration in various Co^{2+} concentration electrolytes.	54
Figure 24. Recombination resistances of cell 6 and cell 8 against V_{ecb}	55

Figure 25. Light intensity dependence of (a) the open-circuit voltage and (b-d) the current density under short-circuit conditions for DSC with various TBP concentration in different $\text{Co}^{2+/3+}$ concentrations.....	56
Figure 26. The diffusion limiting currents of 0.1 M Co^{I} electrolyte with 0.1 M and 0.5 M TBP concentrations determined from PEDOT symmetric cells at a scan rate of 10 mV/s. Every 20 th data point is marked with a symbol.	58
Figure 27. Spectra of IPCE for DSCs employing 0.1M Co^{II} electrolyte with 0.1M and 0.5M TBP concentrations.....	59
Figure 28. Comparison of recombination resistance of various cells as described in Table 2, plotted against V_{ecb}	62
Figure 29. (a) Chemical capacitance (C_{μ}) of devices using 0.1 M Co^{2+} electrolyte with 0.1 M TBP and 0.5 M TBP, plotted against V_{F} . (b) Cyclic voltammogram of $\text{Co}(\text{bpy})_3(\text{TFSI})_2$ with or without the presence of TBP.....	63
Figure 30. Chemical structures of (left) two liquid crystals compounds, 4-cyano-4'-pentylbiphenyl (5CB) and 4-cyano-4'-octylbiphenyl (8CB), and (right) sensitizer L102.	67
Figure 31. Chemical capacitance as a function of corrected potential of the devices using electrolyte E1 to E4. (a) fresh devices (b) 1 day after fabrication.....	68
Figure 32. Cyclic voltammogram of pristine $\text{Co}(\text{bpy})_3(\text{TFSI})_2$ and in the presence of 5CB and 8CB.....	69
Figure 33. Photocurrent-voltage characteristics of devices (after 1 day) under illumination using different electrolyte (light intensity: 100 mW.cm^{-2} , AM1.5G) and IPCE of devices employing E2 and E5. Every 5 th data point is marked with a symbol. ..	70
Figure 34. Conduction band and recombination resistance of fresh cell (solid symbol) and cell after 1 day of storage (open symbol) using E2, E3 and E4. Chemical capacitance (C) and recombination resistance (R_{rec}) are plotted against V_{f} and V_{ecb} , respectively.....	72

Figure 35. Recombination resistance of a collection of DSCs (after 1 day) using different electrolyte.	73
Figure 36. Schematic diagram of TiO ₂ /electrolyte interface showing TBP and 5CB or 8CB as insulating barrier in preventing back reaction between electron in TiO ₂ and Co ³⁺ species in cobalt-complex redox electrolyte.	73
Figure 37. Light intensity dependence of the current density under short-circuit conditions for DSCs (after 1 day) with various Co(II/III) electrolyte.....	74
Figure 38. (a) EIS spectra of devices using E2, E3 and E4 electrolytes measured under illumination at V _{oc} . Symbols represent experimental data and solid lines show the fittings. (b) Stability testing (stored in dark) of DSCs with E8 electrolyte.	75
Figure 39. Chemical structures of N719 sensitizer and coadsorbers (HPA, DPA and ODPa).....	79
Figure 40. (a-c) Photocurrent-voltage characteristics of N719-sensitized devices in which the mesoporous TiO ₂ films are treated with DPA in different solvent system (light intensity: 100 mW.cm ⁻² , AM1.5G). (d-f) IPCE of the respective devices. Every 5 th data point is marked with a symbol.	81
Figure 41. (a) Recombination resistance, (b) transport resistance and (c) charge collection efficiency of the devices with and without DPA-treated TiO ₂ in ethanol.....	83
Figure 42. (a) Photocurrent-voltage characteristics of N719-sensitized devices in which the mesoporous TiO ₂ films are treated with three different alkanephosphonic acids (light intensity: 100 mWcm ⁻² , AM1.5G). (b) Dark current of the devices.	85
Figure 43. (a) IPCE of the devices with and without phosphonic acid treated photoanodes. (b and c) Capacitance and recombination resistance of the devices measured using electrochemical impedance spectroscopy.	86
Figure 44. Chemical structures of C106 sensitizer.....	87

Figure 45. (a) Photocurrent-voltage characteristics and dark currents of (a) N719- and (b) C106-sensitized devices using DPA-treated TiO ₂ electrodes and their control devices. (light intensity: 100mWcm ⁻² , AM1.5G).....	88
Figure 46. IPCE of (a) N719- and (b) C106-sensitized devices using DPA-treated TiO ₂ electrodes and their control devices.	89
Figure 47. Chemical capacitance and recombination resistance of (a,b) N719- and (c,d) C106-sensitized devices.	89
Figure 48. Synthetic routes of 2-(1-isopropyl-imidazol-2-yl)pyridine ligand (py-Im-Y) and cobalt redox couple (MY14).....	93
Figure 49. Chemical structures of (a) Co(bpy) ₃ (PF ₆) ₂ , (b) MY14 and (c) C218 sensitizer.	94
Figure 50. Optical absorption spectra of cobalt(II/III) redox couples in electrolyte. Inset shows the colour of the two electrolyte solutions.	95
Figure 51. (a) Cyclic voltammograms of Co(bpy) ₃ (PF ₆) ₂ and MY14. (b) Schematic energy diagram of C218-sensitized DSCs using MY14 and Co(bpy) ₃ (PF ₆) ₂ as electrolyte.	96
Figure 52. (a) Photocurrent-voltage characteristics and dark currents of C218-sensitized devices with Co(bpy) ₃ (PF ₆) ₂ or MY14 as electrolyte. (light intensity: 100mW.cm ⁻² , AM1.5G). (b) IPCE spectra of C218-sensitized devices with Co(bpy) ₃ (PF ₆) ₂ or MY14 as electrolyte.	97
Figure 53. (a) Chemical capacitance and (b) recombination resistance of C218-sensitized solar cells with Co(bpy)PF ₆ and MY14 as electrolytes.....	98
Figure 54. Photocurrent transient of C218-sensitized DSCs with Co(bpy)PF ₆ and MY14 as electrolytes.	99
Figure 55. Chemical structures of spiro-OMeTAD, FK102 and MY11 dopants.....	103
Figure 56. Synthetic routes of ligand and MY11 dopant.	105

Figure 57. (a) Cyclic voltammogram of spiro-OMeTAD, FK102 and MY11. (b) Schematic energy diagram of $\text{CH}_3\text{NH}_3\text{PbI}_3$ based solar cells using spiro-OMeTAD as hole conductor. The red arrow indicates the driving forces for doping of spiro-OMeTAD using MY11.....	107
Figure 58. (a) UV-vis absorption spectra of spiro-OMeTAD with additives (LiTFSI and TBP) and dopants (FK102 or MY11). Inset shows the enlarged spectra of the oxidized spiro-OMeTAD peak at around 524 nm. (b) Optical absorption of spiro-OMeTAD solution with a gradual increase of dopant concentration.	109
Figure 59. Device configuration of solid state organic inorganic perovskite solar cell: FTO/compact TiO_2 layer/mesoporous TiO_2 layer: $\text{CH}_3\text{NH}_3\text{PbI}_3$ /spiro-OMeTAD/Au....	110
Figure 60. Photocurrent-voltage characteristics and dark currents of $\text{CH}_3\text{NH}_3\text{PbI}_3$ representative devices using spiro-OMeTAD with different dopants (light intensity: 100mWcm^{-2} , AM1.5G).	111
Figure 61. (a) UV-vis absorption spectra of FK102 and MY11 in acetonitrile. (b) IPCE of perovskite-based devices with different dopant concentrations.....	112
Figure 62. Chemical structures of (a) 2-(1 <i>H</i> -imidazol-2-yl)pyridine, (b) 2-(2-pyridyl)benzimidazole, (3) 2,2'-bipyridyl (bpy) and (d) 1,10-phenanthroline (phen)....	118
Figure 63. Proposed ligands for new cobalt(II/III) redox couples.	118
Figure 64. A proposed chemical structure of a metal complex for the synthesis of a dopant with a deeper redox potential.	119

List of Tables

Table 1. List of Co ^{II/III} electrolytes used in DSCs and their redox potentials.....	22
Table 2. <i>J-V</i> characteristics with different TBP concentrations in Co(II/III) electrolyte using PEDOT counter electrode. A total of 24 devices were fabricated and tested.....	52
Table 3. <i>J-V</i> characteristics of DSCs (measured 1 day after fabrication) using various Co(II/III) electrolyte containing different concentration of TBP, 5CB and 8CB as additives. A total of 24 devices were fabricated and tested.	68
Table 4. Charge transfer resistance of DSCs measured at open-circuit potential using different Co(II/III) electrolytes.....	75
Table 5. <i>I-V</i> characteristics of N719-sensitized devices with cobalt-based redox electrolyte. The TiO ₂ photoanode is treated with DPA in different solvents for 1 hour. The ratio of hexane:ethanol is 9:1. A total of 18 devices were fabricated and tested.....	80
Table 6. <i>I-V</i> characteristics of N719-sensitized devices with three different phosphonic acids grafted on mesoporous TiO ₂ . The ratio of solvent is hexane:ethanol is 9:1. A total of 12 devices were fabricated and tested.....	84
Table 7. <i>I-V</i> characteristics of N719 and C106 sensitized devices with and without DPA-treated mesoporous TiO ₂ . A total of 12 devices were fabricated and tested.....	88
Table 8. Comparison of conductivity of undoped and doped spiro-OMeTAD films (with 15.8 mol% FK102 or MY11) on glass substrates.	110
Table 9. <i>I-V</i> characteristics of CH ₃ NH ₃ PbI ₃ devices using different dopants for spiro-OMeTAD. A total of 12 devices were fabricated and tested.	111

List of Abbreviations

CE	Counter Electrode
DSC	Dye-sensitized Solar Cell
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FF	Fill Factor
FTO	Fluorinated Tin Oxide
HOMO	Highest Occupied Molecular Orbital
HTM	Hole Transport Material
IPCE	Incident Photon-to-Collected Electron
J_{sc}	Short circuit current density
LUMO	Lowest Unoccupied Molecular Orbital
η_{coll}	Electron Collection Efficiency
η_{inj}	Electron Injection Efficiency
η_{LHE}	Light Harvesting Efficiency
PCE	Power Conversion Efficiency
V_{oc}	Open-circuit Voltage

Chapter 1

Introduction

1.1 Background and motivation

Energy crisis. At present, the population of the world is around 7 billion which is expected to increase to 9 billion by 2050 and 10 billion by 2100 [1, 2]. The resulting rise in energy consumption is exacerbated by the need for nations to develop diversified economies whilst maintaining political stability; with future increases in the demand for energy resources mainly based on non-renewable energy resources such as oil and gas. However, this heavy dependence on non-renewable resources leads to environmental concerns such as depletion of the non-renewable resources and intensified greenhouse effects caused by releasing more carbon dioxide into the environment.

Annual global power consumption currently stands at approximately 15 TW (1 TW = 10^{12} W) [3]. To address this demand, the utilization of clean and renewable energy sources such as solar, marine, wind, biomass and geothermal energy must be encouraged. This demand for energy is expected to keep on increasing as the global population increases. Among all the above mentioned renewable resources, solar energy is the only one that can meet this level of demand. The sun delivers 174,000 terawatts each day to the surface of the earth which is over 10,000 times more than the yearly global energy consumption.

Nuclear plants are not feasible on safety grounds in Singapore. Hence, utilization of renewable energy sources such as biogas, waste incineration and solar photovoltaics have become the most popular options as energy resources. Out of these options, solar energy is the most promising renewable energy resources for Singapore, where there is

an average annual solar irradiance of 1,150 kWh/m²/year which is approximately 50% more solar radiation than temperate countries. Thus, photovoltaics has the greatest potential for wider deployment in Singapore.

State of the art. Currently, single crystal silicon solar cells with low band gap energy (1.1 eV) are the paradigm for converting sun light into electricity for which 25% power conversion efficiency has been achieved [4]. However, their expensive and energy intensive manufacturing processes have prompted research into finding alternatives [5, 6]. Over the past decades, there has been an increasing interest in organic electronics and electrochemical devices using relatively cheap inorganic semiconductors for replacing conventional microelectronics. As part of this effort, photovoltaic systems such as molecular and polymer organic solar cells as well as dye-sensitized solar cells (DSCs) have been invented. As one type of mesoscopic solar cells, dye-sensitized solar cells (DSCs) were first reported in 1991 by O'Regan and Grätzel [7]. Subsequently they have attracted great attention due to their low cost of production and a range of promising features that suggest market entry is possible. The idea of DSCs is inspired by the concept of photosynthesis in nature. In DSCs, the light harvesting and charge transport are handled by different components in the system which is similar to the process of photosynthesis wherein photons are absorbed by chlorophyll but this does not contribute directly to the charge transport processes. On the other hand, this differs from conventional photovoltaic (PV) devices where the light absorbing and charge transport are both performed by the semiconductor.

Wide band gap metal oxide semiconductors such as TiO₂ (3.2 eV) and ZnO (3.3 eV) are commonly used for PV devices. Their photochemical stability is another factor making them promising candidates for photovoltaic cells. Interestingly, the absorption spectrum can be enlarged by attaching photosensitizers, which normally contain organic chromophores in their chemical structures which lead to higher light harvesting

capability [8]. Photoelectrochemical studies on sensitized polycrystalline titanium dioxide (TiO_2) electrode have shown high incident photon to current conversion efficiency and prompted investigations into the possibility of applying the idea of sensitization into PV devices [9, 10]. Later on, in the 1980s, pioneering work in combining ruthenium based sensitizers and TiO_2 electrode with high surface area revealed an unprecedentedly high visible light to electricity conversion efficiency which lead to the prototype DSCs [11]. Serious attention was only paid to DSCs starting from 1991 when O'Regan and Grätzel made an innovative breakthrough by reporting the use of a nanocrystalline mesoporous TiO_2 electrode, which yielded a power conversion efficiency of over 7% in this photoelectrochemical system. The use of a mesoporous TiO_2 electrode with a high surface area allows higher dye loading and facilitates the diffusion of redox mediators, generating impressively high photocurrent density at that time. To date, the mesoporous TiO_2 electrode remains the best choice for creating high efficiency solar cells.

Loss in potential. Since the successful achievement of high efficiency devices, tremendous effort has been made into developing an alternative semiconductor as electrode, modifying the semiconductor nanostructures, synthesizing stable low band gap inorganic and organic sensitizers with high molar extinction coefficients, replacing conventional platinum electrodes with low cost alternatives as well as substituting the original iodide/triiodide electrolyte with other redox mediators or solid state hole conductors to ameliorate the overall efficiency. It is well-known that a conversion efficiency of 30% is the maximum efficiency for single junction solar cells using light absorbing material with 1.1 eV based on the Shockley-Queisser limit [12]. In the DSCs, employing iodide/triiodide as electrolyte, the main limiting factor to reach the optimal efficiency is the loss in overpotential which can be simply defined as the difference

between the band gap of the photosensitizer and the open-circuit potential (V_{oc}) of the device (see Figure 1).

Figure 1. Schematic energy level of typical DSCs. V_{oc} is determined by the difference Fermi level (E_F) of TiO_2 and the redox potential of the electrolyte. Overpotential is required for electron injection and dye regeneration.

Generally, there are two types of overpotential involved in driving the DSCs, namely the overpotentials for electron injection and for dye regeneration. Although there is no precise value for the overpotential for electron injection, it is commonly believed a value of 100 – 150 mV is needed to inject electrons into the conduction band of the semiconductor [13]. However, the major loss in potential originates from the overpotential for dye regeneration which was found to be around 600 – 700 mV depending on the highest occupied molecular orbital (HOMO) of the photosensitizer. Out of this 700 mV loss in potential, only 250 – 300 mV is required for dye regeneration [14, 15]. These two losses in potential greatly limit the overall attainable efficiency of the device, Figure 2.

Figure 2. Maximum obtainable power conversion efficiencies versus absorption onset for various photovoltage losses. The model assumes an external quantum efficiency of 90% with the rise from the onset of absorption occurring over a range of 50 nm and a constant fill factor of 0.75 [16].

Ways to reduce loss in overpotential and its challenging parts. A feasible way to reduce the loss in overpotential is to develop new redox couples exhibiting more positive redox potentials which results in the reduction in the overpotential for dye regeneration. Among potential alternative redox electrolytes, the most promising alternatives to the iodide/triiodide electrolyte are cobalt-complex based redox mediators that possess low molar absorptivities and tunable redox potentials [17]. The impact of employing cobalt-based electrolyte is reflected in the significant enhancement in V_{oc} which arises from the reduction in overpotential for dye regeneration [18, 19]. Notably, a record power conversion efficiency of 13% has been accomplished by combining zinc-porphyrin sensitizers and tris(2,2'-bipyridyl)cobalt(II/III) ($[Co(bpy)_3]^{2+/3+}$) redox shuttles [20].

However, the most challenging part in generating high efficiency solar using cobalt-based redox electrolytes is to reduce the interfacial recombination between electrons in the conduction band of TiO_2 and the oxidized redox species in the electrolyte, as the recombination could be two orders of magnitude higher than that in the iodide/triiodide redox system [21]. Device engineering such as using compact TiO_2 underlayers and surface passivation is crucial in attaining efficient solar cells with high

V_{oc} . Therefore, interfacial engineering has become an important aspect in the research area of Co(II/III)-mediated DSCs. Another potential bottleneck of utilizing cobalt-based electrolyte is its slower diffusion due to its bulkier molecular size. This issue has to be overcome in designing new cobalt complex to avoid the mass transport limitation which directly reduces the short-circuit current (J_{sc}), leading to lower device efficiency. Owing to the key issues mentioned above, much research has focused on developing new strategies to reduce the interfacial recombination including using new electrolyte additives, surface passivation of the semiconductor (normally TiO_2) and development of novel cobalt-based redox mediators should be persisted to further enhance the V_{oc} which is considered as one of the more significant ways to ameliorate the overall power conversion efficiency in Co(II/III)-mediated solar cells.

In this thesis, higher power conversion efficiency is demonstrated by controlling the interfacial recombination *via* modulating the electrolyte additive, use of interfacial passivation and by developing new cobalt redox shuttles as well as cobalt dopant for solid state hole transporting material (HTM) for high voltage devices. The first work discussed the investigation of the influence of modulating electrolyte additives on the interfacial recombination which is the major cause of having low V_{oc} . Cyanobiphenyl based organic compounds are also introduced as electrolyte additives for Co(II/III)-mediated DSCs for the first time to further reduce the recapture of photoinjected electron by Co^{3+} species in electrolyte. Other than the electrolyte additives, surface passivation for preventing the undesired back reaction using alkanephosphonic acids will also be discussed. The concept of creating insulating barriers on TiO_2 surface is also transferred to the redox mediators by developing new cobalt complex embedded with steric bulky groups. The last part of the work discusses the application of novel cobalt-based dopant for molecular HTM in solid state perovskite devices for improving the V_{oc} as well as the conductivity of HTM.

1.2 Thesis objectives and scope

The research focus in this thesis is to study the importance of reducing interfacial recombination *via* the investigation of electrolyte additives, surface passivation and new cobalt redox shuttles which lead to higher V_{oc} . Chemical doping using new cobalt dopant in organic HTM in solid state perovskite solar cell will also be investigated. The main objectives and scopes of this thesis are summarized as follows:

1. Retarding interfacial recombination and minimizing mass transport limitation *via* modulating electrolyte additives in Co(II/III) redox electrolyte.

To reduce the overpotential for dye regeneration, cobalt-based redox mediators are utilized to replace the conventional iodide/triiodide electrolyte for promoting higher V_{oc} . However, the electrolyte additives used in cobalt-based electrolyte are inherited from the iodide/triiodide electrolyte which may not be ideal for cobalt(II/III) electrolytes. For this purpose, a detailed study of the effect of electrolyte additives on the interfacial recombination, mass transport limitation and its photovoltaic effect was conducted. In addition, two cyanobiphenyl organic molecules, also deliberately chosen based on their molecular structures, were introduced into the Co(II/III) redox electrolyte in order to further improve the photovoltage of the devices and ultimately produce a device with higher efficiency. The reasons for the improved device performances were revealed through electrochemical impedance spectroscopy and photoelectrochemical characterizations.

2. Preventing unfavourable electron recapture *via* surface passivation of TiO₂ and structural modification of cobalt(II/III) redox mediators.

The most severe interfacial recombination for Co(II/III)-mediated DSCs occurs between the electron in TiO₂ and the oxidized species of cobalt redox couples. To address this issue, the mesoporous TiO₂ surface was passivated by a series of phosphonic acids bearing long alkyl chains which act as insulating barriers impeding the undesired back reaction. The charge collection efficiency was investigated by measuring impedance spectroscopy while the impacts of solvents and photosensitizer on photovoltaic performances were also ascertained. Moreover, the redox potential tunability and structural modification of cobalt redox couples were performed by incorporating isopropyl groups onto imidazolylpyridine bidentate ligands for hindering the interfacial recombination. The diffusivity of the redox shuttles was also examined using photocurrent transient measurements.

3. Enhancing charge transfer of spiro-OMeTAD using p-type dopant with deep redox potential in solid-state perovskite solar cells

Transformation of liquid state DSCs into solid state DSCs involves the replacement of the liquid electrolyte by a solid hole conductor, 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)9,9'-spirobifluorene (spiro-OMeTAD), exhibiting more positive redox potential than iodide/triiodide and cobalt(II/III) based electrolytes which further reduces the loss in overpotential. However, the pristine form of this hole conductor possesses low conductivity which is detrimental to the device performances. To overcome this limitation, a new cobalt based dopant with high redox potential was designed which is able to dope a wide range of hole conductors used in photovoltaic devices. The charge transfer reactions between spiro-OMeTAD and cobalt dopant was

monitored through optical absorption measurement while the conductivity of hole conducting film was examined by 4 probe conductivity measurement. The J - V characteristics were compared to control devices using the conventional dopant, FK102.

1.3 Thesis organization

This thesis consists of 9 chapters. In chapter 1, the background of the invention of dye-sensitized solar cells and the motivation for promoting higher photovoltage of the solar devices is presented. The strategies used in this project for photovoltage enhancement are also highlighted, followed by the contribution of this thesis.

In chapter 2, the working principle of DSCs is described. The photovoltaic parameters affecting the power conversion efficiency are also discussed. The advantages and disadvantages of using Co(II/III) electrolyte are highlighted. Progress in DSCs using cobalt electrolytes and the related perovskite solar cells are also reviewed.

In chapter 3, the material preparations including synthesis of cobalt(II/III) redox mediators, cobalt dopant for spiro-OMeTAD, methylammonium iodide and electrodeposition of poly(3,4-ethylenedioxythiophene) counter electrode were described. The methods of solar cell fabrication for both liquid state DSCs and solid state perovskite devices are also presented.

In chapter 4, the results of investigating the interfacial recombination and mass transport limitation in Co(II/III) electrolyte are shown. The photovoltage of devices was monitored by modulating the electrolyte composition of TBP and cobalt(II/III) redox couples.

In chapter 5, the results of improved recombination resistance by introducing cyanobiphenyl organic molecules as electrolyte additives in cobalt-based electrolyte are presented. The adsorption of these additives onto the surface of semiconductor and its

effects in preventing the interfacial recombination were revealed by using electrochemical impedance spectroscopy. The stability of the devices is also discussed.

In chapter 6, the results of higher V_{oc} through surface passivation using alkanephosphonic acid are shown. The improved charge collection efficiency and recombination resistance are shown by impedance spectroscopy. The effect of surface passivation in the devices using various sensitizers is also demonstrated.

In chapter 7, tunability of redox potential and reduced back reaction are discussed by employing newly synthesized cobalt complexes as redox couples. The comparison to the device using highly efficient $Co^{2+/3+}(bpy)$ redox electrolyte is also discussed. The electron recapture and mass transport property in this new electrolyte are presented using impedance spectroscopy and photocurrent transient measurement.

In chapter 8, the importance of developing new cobalt dopant with deep redox potential for spiro-OMeTAD is highlighted. Better charge transfer between spiro-OMeTAD and dopant is also rationalized by monitoring its optical absorption and conductivity. The photovoltaic performances are systematically compared and discussed.

Chapter 9 shows the summary of the entire project in this thesis. Future ways for reducing interfacial recombination and promoting V_{oc} in DSCs are also suggested.

1.4 Contribution of thesis

Scientific contributions achieved in this PhD project include:

- 1) Detailed and systematic study on interfacial recombination and mass transport property of Co(II/III) redox system is conducted through modulating the electrolyte additives where an unforeseen mass transport limitation is observed due to the viscous nature of electrolyte additive.
- 2) For the first time, cyanobiphenyl based organic molecules are introduced as electrolyte additives in DSCs, realising the photovoltage enhancement from their reduced interfacial recombination.
- 3) Significant passivation of the recombination interface is attained by using alkanephosphonic acids which leads to higher recombination resistance and charge collection efficiency.
- 4) New cobalt complex bearing bulky hindrance is synthesized and utilized as redox electrolyte for retarding the interfacial recombination without inducing mass transport limitation.
- 5) New cobalt(III) complex with deep redox potential is successfully synthesized as chemical dopant for organic HTMs. Its deep redox potential offers the possibility of doping a wide range of HTMs for higher V_{oc} as well as improved conductivity.

Chapter 2

Literature Review

In section 1.1, a brief background of dye-sensitized solar cells (DSCs) is described. Here, the operating principles and key factors affecting the performance of DSCs will be presented. The innovation of iodide/triiodide electrolyte into cobalt-based electrolyte and the recent technological advancement in solid state DSCs (ssDSCs) will also be introduced.

2.1 Dye-sensitized solar cells (DSCs) and its operating principle

While the current solar cell industry is dominated by the silicon-based solar cells, scientific research is now focussing on solution processable solar cells which are based on low-cost materials as well as cheap and high throughput manufacturing technologies. The DSCs have been regarded as the most promising candidate in fulfilling the list of requirements.

DSCs which are also referred to as “Grätzel cells”, began to receive attention after the efficiency breakthrough in 1991 where O'Regan and Grätzel announced the use of nanocrystalline mesoporous TiO_2 electrode and achieved a 7% of power conversion efficiency. The common principal processes for any photovoltaics include light absorption, generation and transport of charges towards the electrodes. Unlike conventional p-n junction solar cells, DSC is a photoelectrochemical cell where the light absorption and electron/hole transport are taken place in specifically designed components which is inspired by the photosynthesis in nature. Therefore, the cell configuration and working mechanism are different from the conventional inorganic semiconductor solar cells. The main component of the system is a layer of wide band gap

mesoporous semiconductor, usually TiO_2 , which is deposited on top of a fluorine-doped tin oxide (FTO) coated glass substrate. The size of TiO_2 nanoparticle is normally ~ 20 nm in diameter. A monolayer of dye molecules (metal-based or organic-based sensitizers) for light harvesting is attached to the surface of the nanometer-sized TiO_2 particles *via* the anchoring groups in their molecular structures, *i.e.* carboxylate or phosphonate functional groups [22, 23]. Upon light absorption, the sensitizer is photoexcited and, with appropriate energy level alignment, leads to the injection of an electron into the conduction band of the semiconductor and subsequently the transportation to working electrode. The photooxidized sensitizer is regenerated to its ground state by electron donation from the redox electrolyte which commonly contains an I^-/I_3^- redox couple in organic solvent. The I_3^- ions formed during the dye regeneration diffuse through the electrolyte to the platinum-coated counter electrode and the regenerating cycle is completed by the reduction of I_3^- to I^- at platinum catalyst. A schematic representation of DSCs is shown in Figure 3 for a better understanding of the device configuration.

Figure 3. Schematic structure of DSCs.

In DSCs, the device performance is mostly dependent on the energy level alignment of each component as well as the kinetics of charge separation and charge

transfer processes. Figure 4 shows an energy level diagram with the charge transfer processes occurring in liquid state DSCs.

Figure 4. Simple energy level diagram with charge transfer processes occurring in DSCs under illumination.

The basic charge transfer processes occurred in DSCs include:

1. Photoexcitation of sensitizer
2. Excited state decay of sensitizer
3. Electron injection into semiconductor (TiO_2)
4. Regeneration of sensitizer by electron transfer from reduced form of redox mediators
5. Reduction of oxidized form of redox mediators
6. Back electron transfer from TiO_2 to oxidized sensitizer
7. Recombination of injected electron in TiO_2 with oxidized form of redox mediators.

Under illumination, photoexcitation of sensitizer (reaction 1) occurs whereby an electron is promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The LUMO energy level of sensitizer should

always be higher than the conduction band edge of the TiO₂ semiconductor to ensure effective electron injection (reaction 3). The electron ignition process typically takes place in the femtosecond timescales [24-26], however, the excited state lifetime of Ru-based sensitizers is generally 20-60 ns [27]. Therefore, dye relaxation (reaction 2) is not a competing process. The oxidized sensitizer is subsequently regenerated by the electron donor (I⁻) in the electrolyte on a microsecond timescale (reaction 4), meanwhile, the holes (I₃⁺) are transported and reduced by a platinum electrocatalyst at the counter electrode (reaction 5). The regenerated sensitizer is then available to absorb another photon. When more electrons are injected into the conduction band, the quasi-Fermi level of the semiconductor will be shifted upward. The maximum open-circuit voltage (V_{oc}) is determined by the difference between the quasi-Fermi level and the redox potential of the redox couple. Generally, two commonly seen undesirable reactions may take place where electrons in the conduction band may recombine with the electrolyte acceptor (reaction 6) and oxidized sensitizer (reaction 7) in microsecond and millisecond timescales, respectively [28].

2.2 Evaluation of power conversion efficiency

The power conversion efficiency (PCE, η) of DSCs is determined by the short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}) and fill factor (FF) [28]. The PCE of a DSC is defined as the ratio of maximum power output, P_{max}, and the incident solar power, P_{in}. The maximum power output is the product of J_{sc}, V_{oc} and FF. Hence, the PCE can be described as:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

A typical I - V and P - V curve of photovoltaic device is illustrated in Figure 5. Understanding of the parameters affecting the PCE helps in further improving the device performances [29].

Figure 5. Typical I-V and P-V curve of a photovoltaic device.

Short-circuit photocurrent density, J_{sc}

J_{sc} is obtained in the condition when the applied potential is zero. J_{sc} is linearly proportional to the light intensity. Basically, it is affected by the light harvesting of sensitizer, charge collection by semiconductor, charge injection to semiconductor and regeneration of the sensitizers. J_{sc} of a solar device can be estimated from

$$J_{sc} = \int IPCE(\lambda) e \Phi_{ph,AM1.5G}(\lambda) d\lambda$$

where IPCE is the incident photon to current conversion efficiency, e is the elementary charge and $\Phi_{ph,AM1.5G}$ is the photon flux at a light intensity of AM 1.5 G, 100 mW.cm^{-2} . Therefore, IPCE can be indicated as

$$IPCE(\lambda) = \eta_{LHE} \times \eta_{inj} \times \eta_{coll} \times \eta_{reg}$$

where η_{LHE} is light harvesting efficiency, η_{inj} is electron injection efficiency, η_{coll} is collection efficiency and η_{reg} is regeneration efficiency [30].

IPCE values correlate to the photocurrent density obtained in the external circuit under monochromatic illumination of the cell divided by the photon flux that strikes the

cell. IPCE values give information about the monochromatic quantum efficiencies of solar cell. Thus, IPCE can be also denoted by

$$\text{IPCE (\%)} = \frac{1240 \text{ (eV nm)} \cdot J_{sc} \text{ (\mu A cm}^{-2}\text{)}}{\lambda \text{ (nm)} \cdot \phi \text{ (\mu W cm}^{-2}\text{)}} \times 100$$

where J_{sc} is short-circuit photocurrent density for monochromatic illumination, λ is wavelength and ϕ is intensity.

Open-circuit voltage, V_{oc}

When the contacts of the device are open or isolated, the potential difference is referred as V_{oc} . It is the applied bias at where there is no external current flow between two contacts of the solar device. For ideal diode,

$$V_{oc} = \frac{kT}{q} \ln \left(\frac{J_{sc}}{J_0} + 1 \right)$$

Therefore, V_{oc} increases logarithmically with photocurrent density and light intensity [28].

Fill factor, FF

The fill factor is defined by the ratio of the maximum power (P_{max}) of the solar cell per unit area divided by J_{sc} and V_{oc} accordingly [31]. The maximum power is the product of the photocurrent and photovoltage at the voltage where the power output of the cell is maximal. The ideal FF is 1, however, it cannot be achieved in practical due to the presence of various loss mechanisms in DSCs such as charge recombination.

$$FF = \frac{P_{max}}{J_{sc} \cdot V_{oc}}$$

2.3 Redox electrolyte

2.3.1 Iodide/triiodide electrolyte

The electrolyte plays an important role in DSCs for electron and hole transport. Since 1991, the I/I_3^- redox couple has become the standard in high efficiency DSCs [7]. To date, the highest recorded certified efficiency DSCs (11.9%) used an I/I_3^- redox electrolyte[32]. This redox couple is still the favourite choice for many researchers due to its slow recombination between conduction band electrons and oxidized species of redox shuttles (I_3^-) [33, 34] and high diffusion rate through mesoporous TiO_2 [15], presenting promising solar energy conversion.

Under illumination, sensitizers are photoexcited and electrons are injected into the conduction band edge of the semiconductor. The oxidized sensitizers are subsequently regenerated by I^- (reduced species) in the electrolyte. The sensitizer regeneration leads to the formation of diiodide anions ($I_2^{\bullet-}$). The formation of this radical was investigated by nanosecond-laser spectroscopy and pseudo-steady-state photoinduced absorption spectroscopy. The sensitizer regeneration process can be summarized as follows.

Once the excited sensitizer has injected one electron into the conduction band of the semiconductor, oxidized sensitizer subsequently reacts with I^- , leading to the formation of intermediate complex ($S^{\bullet\bullet}I$) [35]. This intermediate complex dissociates when another I^- approaches, forming the regenerated sensitizer (S) and diiodide anions ($I_2^{\bullet-}$). The regeneration is completed when two diiodide radicals combine to form I_3^- and I^- anions.

Another possible regeneration pathway occurs when electron injection is relatively slow or in the presence of high concentration of I^- . The excited sensitizer is first reduced by I^- , forming reduced sensitizer (S^-) and iodine radical ($I^\bullet$) which will react with I^- to give $I_2^{\bullet -}$ [36]. The reduced sensitizer will either inject an electron into conduction band of semiconductor [37] or recombine with I_3^- [38], leaving regenerated sensitizer.

2.3.2 Limitation of iodide/triiodide redox system

Though the classical I^-/I_3^- redox mediator is still one of the best redox systems employed in DSCs, some drawbacks presented by it limit the overall efficiency.

Firstly, I^-/I_3^- redox electrolyte possesses a strong yellowish brown colour and so tends to compete with photosensitizers in light absorption. Figure 6 illustrates the UV-Vis absorption of I^-/I_3^- redox electrolyte. It can be noticed that triiodide (I_3^-) has two absorption bands in the ultraviolet region with maxima at 291 nm ($\epsilon = 42500 \text{ M}^{-1}\text{cm}^{-1}$) and 361 nm ($\epsilon = 22200 \text{ M}^{-1}\text{cm}^{-1}$) in acetonitrile at room temperature while iodide (I^-) has an absorption maxima at 208 nm ($\epsilon = 20800 \text{ M}^{-1}\text{cm}^{-1}$) and 246 nm ($\epsilon = 16300 \text{ M}^{-1}\text{cm}^{-1}$). The absorption of I^-/I_3^- redox electrolyte from 350 nm to 450 nm overlaps with part of the the absorption of the sensitizers, reducing photocurrent and ultimately lowering the power conversion efficiency.

Figure 6. UV-Vis absorption spectra of TBAI, TBAI₃ and the iodine radical anion (I₂^{•-}) in acetonitrile [14].

Secondly, redox potential of I⁻/I₃⁻ electrolyte system is only 0.35 V (*vs* normal hydrogen electrode, NHE) which results in potential loss in DSCs, limiting the overall efficiency. Generally, regeneration of ruthenium-based sensitizers with I⁻/I₃⁻ redox mediators leads to around 700 mV of photovoltage loss, with over 300 mV of that is directly related to the internal reaction within the I⁻/I₃⁻ redox couples [14]. Dye regeneration is most probably the largest potential loss in the devices. With 750 mV potential loss in typical ruthenium complex sensitized DSCs, the overall power conversion efficiency is limited to 13.8%. Figure 2 highlights the importance of reducing the loss in overpotential for achieving high efficiency photovoltaic devices. To reduce the overpotential for dye regeneration, alternative redox couples with more positive redox potentials are essential.

2.3.3 Co(II/III) redox couples for DSCs

Chemical and physical properties. Photovoltaic loss in DSCs using I⁻/I₃⁻ redox couples is mainly due to its absorptivity and photovoltage loss. Awareness of the limitations in this redox system encourages the finding of alternative redox mediators. Thus, minimizing photovoltage loss within the devices becomes the most challenging task for the research in DSCs.

The use of single electron redox mediators offers a direct way for dye regeneration. Design of alternative redox couples for DSCs should meet the requirements: 1) its redox potential should be more positive than that of I/I_3^- to gain higher potential 2) its redox potential should be more negative than the HOMO energy level of photosensitizer, ensuring efficient regeneration.

The emergence of cobalt^{II/III} redox couples offers opportunities to enhance the photovoltaic performance by improving V_{oc} of the device. Generally, Co^{II} complexes (normally high spin state) are responsible for dye regeneration due to their higher reactivity compared to Co^{III} complexes [19]. Co^{III} complexes (normally low spin) are subsequently reduced to Co^{II} complexes at the counter electrodes (Figure 7).

Figure 7. Outer-orbital diagram of high spin Co^{II} ion and low spin Co^{III} ion.

The first advantage of $Co^{II/III}$ redox electrolyte is its less competitive absorption compared to I/I_3^- redox couples. Figure 8 illustrates the UV-Vis absorption spectra of I/I_3^- , $[Co(bpy)_3]^{II/III}$ and N3 dye in mesoporous TiO_2 films. The less absorption from 350-450 nm in $Co^{II/III}$ redox electrolyte will result in higher photocurrent densities in the devices.

Figure 8. UV-Vis absorption spectra of I/I_3^- , $[Co(bpy)_3]^{II/III}$ and N3 dye in mesoporous TiO_2 films [17].

Tunable redox potential. The most interesting advantage of Co^{II/III} redox shuttles is their tunable redox potential. The redox potential of the cobalt complex can be tuned by tailoring the coordinating ligands. A list of cobalt complexes used in DSCs and their redox potentials are summarized in Table 1.

Table 1. List of Co^{II/III} electrolytes used in DSCs and their redox potentials.

Molecular structure	Redox potential / [reference]	Molecular structure	Redox potential / [reference]
<p>Co(dbbp)₂</p>	0.39V ^a / [18, 39]	<p>Co(py-pz)₃, R = H Co(py-pzMe₂)₃, R = Cl</p>	Co(py-pz) ₃ , 0.32V ^c / [40] Co(py-pzMe ₂) ₃ , 0.34V ^c / [40]
<p>Co(abpn)</p>	0.41V ^b / [41]	<p>Co(bpy-pz)₂</p>	0.86V ^b / [40, 42-44]
<p>Co(bpy)₃, R = H Co(bpy-Me)₃, R = Me Co(bpy-OMe)₃, R = OMe Co(bpy-dtb)₃, R = <i>t</i>-butyl Co(bpy-Cl)₃, R = Cl</p>	Co(bpy) ₃ , 0.56V ^b / [45-48] Co(bpy-Me) ₃ , 0.43V ^b / [45, 47] Co(bpy-OMe) ₃ , -0.28V ^c / [49] Co(bpy-dtb) ₃ , -0.26V ^c / [45, 49] Co(bpy-Cl) ₃ , 0.17V ^c / [40]	<p>Co(PY5Me₂)(tBP)</p> <p>Co(PY5Me₂)(NMBI)</p>	0.78V ^b / [50] 0.71V ^b / [50]

<p>Co(phen)₃, R = H Co(phen-Cl)₃, R = Cl Co(phen-NO₂)₃, R = NO₂</p>	<p>Co(phen)₃, 0.62V^b/ [45, 47]</p> <p>Co(phen-Cl)₃, 0.72V^b/ [47]</p> <p>Co(phen-NO₂)₃, 0.85V^b/ [47]</p>	<p>Co(tpy)₂, R and R' = H Co(tpy-ttb)₂, R and R' = <i>t</i>-butyl Co(tpy-Cl)₂, R = H, R' = Cl</p>	<p>Co(tpy)₃, 0.50V^b/ [51]</p> <p>Co(tpy-ttb)₂, -0.32V^c/ [45, 49]</p> <p>Co(tpy-Cl)₂, 0.63V^b/ [51]</p>
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^a vs. SCE. ^b vs. NHE. ^c vs. Fc/Fc⁺

The first cobalt redox mediator [Co^{II/III}(dbbip)₂, Table 1] used in DSCs was reported in 2001 [39]. Combining with a ruthenium sensitizer (Z316), this new class of redox shuttle yielded 2.2% power conversion efficiency under AM1.5 irradiation (100 mW cm⁻²). In their subsequent work, a series of cobalt redox couples were tested and 4.2% overall efficiency was achieved by using Co^{II/III}(dbbip)₂ with a Z907 ruthenium based sensitizer [18]. A combination of cobalt electrolyte with Ru-based sensitizer may not be the best choice due to the higher recombination rate and slower mass transport behaviour in cobalt electrolytes compared to the iodide/triiodide electrolytes. A recent report combined experimental and computational investigations in order to observe cobalt electrolyte/dye interactions in DSCs. Through ab initio molecular dynamics simulations, it was shown that the formation of a complex between [Co(bpy)₃]³⁺ and the surface-anchored ruthenium sensitizer occurs, resulting in a higher probability of intercepting TiO₂-injected electrons by the oxidized species in the cobalt electrolyte [52].

Organic photosensitizers generally possess higher extinction coefficients than standard ruthenium-based sensitizers. This allows the use of thinner TiO₂ films in order to facilitate the diffusion and reduce the recombination losses in the Co electrolyte. In 2009, a new strategy was adopted, employing terminal alkoxyl chains in the donor part of D- π -A (donor- π -acceptor) sensitizer for reducing the rate of recombination in the devices

[53]. A year later, an efficient sensitizer, D35, was chosen as sensitizers in a device employing a Co electrolyte [46]. This design of organic sensitizer achieved 6.7% power conversion efficiency with more than 0.9 V of open-circuit potential under 1 sun irradiation. This encouraging result was attributed to the use of a high molar extinction coefficient sensitizer, allowing the use of thinner TiO₂ film, which results in reduced recombination losses and also to the insulating effect provided by the butoxy chains in the sensitizer. A similar synthetic approach has been introduced by Grätzel's group in their new organic sensitizer, Y123, which has been used with the Co^{II/III}(bpy-pz)₂ electrolyte and an overall conversion efficiency of 10.0% has been achieved [42]. This synthetic approach was also demonstrated by studying the structural effect between N719 and Z907 ruthenium sensitizers with Co electrolyte where the latter sensitizer contained long alkyl chains [54].

Mass transport limitation. Another issue that concerns researchers is the mass transport limitation in Co electrolytes, which refers to the difficulty of the oxidized species (Co³⁺) to diffuse to the counter electrode in the device after dye regeneration. Elliott *et al.* have studied the mass transport of polypyridyl cobalt complexes in DSCs and found that the diffusion coefficient of Co^{III}(bpy-dtb) is an order slower than for I₃⁻. This difference may be attributed to the larger size, higher viscosity and a possible electrostatic surface interaction of Co electrolyte within the mesoporous TiO₂ film [55]. Other than mass transport limitations, several other fundamental understandings about this promising redox couple are also reported, including the role of electrolyte on charge recombination [41], effects of driving forces in recombination dynamics [56], photovoltaic performance enhancement and limitations [57], transport and interfacial transfer of electrons [58] and effects of driving forces for recombination and regeneration in DSCs [47].

After realising the differences in physical and chemical properties of this newly developed redox mediator and the typical iodide/triiodide electrolyte, researchers started to develop photoanodes with different morphologies and other new materials for counter electrodes that suppress or eliminate the limitations of Co electrolytes in order to achieve higher conversion efficiencies. As mentioned above, the mass transport issue limits the device performance using Co electrolytes due to their larger size and higher viscosity. Increasing porosity and pore size of mesoporous TiO_2 films is thus one of the methods to improve cell efficiency. Park and co-workers have found that photocurrent density can be improved by nearly two times by increasing the porosity from 0.52 to 0.59 despite a 23% decrease in dye loading, as depicted in Figure 9 [59].

Figure 9. (a) Photocurrent density vs. light intensity for different porosity. Transient photocurrent for porosity of (b) 0.52 and (c) 0.59. 1 sun corresponds to 100 mW cm^{-2} [59].

Not only the porosity, but also the morphologies of TiO_2 films can enhance the transport of Co redox mediators in devices. Sung *et al.* employed highly ordered and vertically oriented TiO_2 nanotube (NT) electrodes with large pore sizes (Figure 10) instead of typical TiO_2 nanoparticles (NP) in DSCs using a cobalt bipyridyl redox electrolyte [60]. The mass transport limitation was greatly alleviated and the interfacial contact between Co electrolyte and photoanode was significantly enhanced. The better cell performance was also attributed to longer electron lifetime and diffusion length in the NT electrodes. Recently, Grätzel's group reported a systematic study of the effects of

film thickness, porosity, particle and pore size on diffusion of $\text{Co}^{\text{II/III}}(\text{bpy})_3$ redox couples [61]. It showed that mass transport problems seem to be independent of particle size. Thinner TiO_2 films with large pore sizes and higher porosity are beneficial to Co redox shuttles while insufficient TiCl_4 post-treatment may reduce the photocurrent density of the device.

Figure 10. FESEM images of annealed TiO_2 NT electrodes with 11 μm thickness [60].

Incompatible with Pt counter electrode. Unlike the I^-/I_3^- redox electrolyte, cobalt-complex redox electrolytes do not seem to work well using a typical Pt counter electrode. In 2002, Bignozzi *et al.* synthesized a series of cobalt complexes and cyclic voltammetric studies showed a dramatic surface dependence of their electron-transfer kinetics. Their electrochemical results also led to the conclusion that gold and carbon outperform platinum as cathode materials in DSCs [45]. They also reported the first screen-printed carbon counter electrode for cobalt-based electrolyte used in DSCs [62]. Grätzel and co-workers reported extraordinary properties of graphene nanoplatelets (GNP) used as an electrocatalyst for $\text{Co}(\text{bpy})^{\text{II/III}}$ redox mediators [63]. Charge transfer resistance (R_{ct}) at the Pt counter electrode was originally $5.5 \Omega\text{cm}^2$ in the first cycle and gradually increased up to $19.3 \Omega\text{cm}^2$ in the 10th cycle. However, a GNP counter electrode exhibited a R_{ct} of $3.3 \Omega\text{cm}^2$, independent of cycle history (Figure 11). Poly(3,4-ethylenedioxythiophene) (PEDOT) is also a superior alternative to the conventional Pt counter electrode used in DSCs. The lower interfacial charge-transfer resistance at the

counter electrode in DSCs based on cobalt-complexes redox shuttles, using PEDOT as electrocatalyst, was highlighted in the work of Grätzel. Due to much lower R_{ct} , the improved fill factors and linear response of short circuit photo-current density led to an excellent power conversion efficiency of 10.3 % [64]. These findings show that GNP and PEDOT counter electrodes appear to be a very promising alternatives to the Pt counter electrode in DSCs using cobalt-complex based electrolytes.

Figure 11. Cycling stability of symmetrical dummy cells with Pt-FTO (left) electrodes and GNP-FTO (G96) electrodes (right) in acetonitrile solution of $\text{Co}^{\text{II/III}}(\text{bpy})_3$ [63].

2.4 Surface passivation

In DSCs, numerous charge transfer processes occur at the interface between the dye-sensitized TiO_2 layer and the redox electrolyte [28]. These charge transfer processes include the electron injection from photon-excited dyes to the conduction band of TiO_2 , the regeneration of dyes and unfavourable processes such as the electron recombination of injected electrons in the TiO_2 film with oxidized redox mediator in the electrolyte or oxidized dyes. Importantly, sufficient passivation of the uncovered TiO_2 surface could retard the interfacial charge recombination process between electrons in the TiO_2 with oxidized species of redox mediator in the electrolyte which leads to the enhancement in

V_{oc}. Thus, effective interfacial engineering can greatly improve the power conversion efficiency of DSCs.

Surface coating

The effective surface coating on TiO₂ surface in DSCs can bring several advantages such as retarding electron recombination of electrons in TiO₂ in electrolyte [65], improving inter-connections of TiO₂ particles for better electron transport [66], increasing charge separation efficiency [67], strengthening dye adsorption and reducing surface traps states [68]. For instance, surface passivation of mesoporous TiO₂ nanoparticles with a wider bandgap metal oxides or insulating metal oxides is a popular strategy in improving V_{oc} of DSCs. The deposited thin layer of metal oxides serves as a blocking layer to suppress the undesired recombination reaction and leads to higher V_{oc} of DSCs. Furthermore, MgO was another frequently used wide bandgap material in forming TiO₂/MgO or SnO₂/MgO core-shell structures for photoanodes whereby the recombination of injected electrons and holes in the electrolyte were greatly reduced [69]. In addition, other metal oxides such as Nb₂O₅ and ZrO₂ were also used as passivation layer on the TiO₂ layer for enhancing the V_{oc} of DSCs to a different extent [70, 71].

However, the main disadvantage of employing this method is that a thicker or inhomogeneous passivation layer of metal oxide could possibly reduce the electron injection efficiency from the photo-excited dyes to the conduction band of TiO₂. Therefore, the electronic property of the deposited metal oxides and their depositing procedures become essential for achieving efficient DSCs.

Coadsorbent

In DSCs, coadsorbents are referred to the compounds that are introduced in the dye loading process in which the coadsorbents attached on to the surface of mesoporous TiO₂ together with dyes. In general, coadsorbents should be wide bandgap organic

compounds which have low light absorption in order to avoid the competition in light harvesting with dye molecules. Usually, coadsorbents facilitate the organization and orientation of the adsorbed dye molecules by occupying spaces between dye molecules and reduce dye aggregation [72].

Deoxycholic acid (DCA) is one of the commonly used coadsorbent in retarding dye aggregation in DSCs [73]. It was revealed that the addition of DCA improves the V_{oc} of the devices. Another derivative, chenodeoxycholic acid (CDCA), was also used mainly in DSCs in order to hinder the formation of dye aggregates and a higher photocurrent was achieved compared to those without CDCA [74]. The addition of CDCA could also lead to higher photovoltage of the devices which was attributed to the shift of the conduction band edge of TiO_2 . In addition, phosphonate compounds could also bind strongly to the TiO_2 surface and were also employed as coadsorbents in DSCs. One of the representative compounds is dineohexyl phosphinic acid (DINHOP) [75]. The two neohexyl substituents in DINHOP act as insulating and hydrophobic layers in preventing the approach of oxidized species in the electrolyte to the surface of TiO_2 . The effective interfacial engineering by using this coadsorbent greatly reduces the rate of interfacial recombination and lead to photovoltage enhancement in DSCs.

Although the complete mechanism of reduced interfacial recombination by coadsorbents is not clear yet, the reasons for enhanced photovoltaic performance are generally ascribed as follows: (1) insulating surface passivation on TiO_2 suppress the interfacial recombination between injected electrons and oxidized redox mediator in the electrolyte; (2) reduction of the dye aggregation on the TiO_2 surface and (3) shift of the conduction band edge of TiO_2 .

2.5 Cobalt dopants for spiro-OMeTAD

Doping of organic semiconductors is considered an efficient way to control their charge carrier density. Charge transfer reactions occur between organic host and the dopant depending on their ionization energy levels. The dopant can donate (n-type doping) or accept (p-type doping) electrons to/from the organic host, leaving it in a reduced or oxidized form.

Inorganic dopants such as molybdenum trioxide (MoO_3) and tungsten oxide (WO_3) have been intensively studied in their application as p-type dopants [76-79], however, their poor solubility is a drawback for solution processed application. In the pioneering work for ssDSCs, $\text{N}(\text{PhBr})_3\text{SbCl}_6$ was introduced as a chemical dopant for spiro-OMeTAD and a power conversion efficiency of 0.74% was obtained [80]. Studies have also shown that the oxidized spiro-OMeTAD can also be generated in the presence of molecular oxygen under illumination [81]. However, the devices fabricated from doping the spiro-OMeTAD using molecular oxygen could suffer from reproducibility and makes the fabrication processes more challenging. Therefore, chemical doping for spiro-OMeTAD becomes essential.

Tris(2-(1*H*-pyrazol-1-yl)pyridine)cobalt(III) tris-(hexafluorophosphate), FK102, has been used for the first time as a p-type dopant for organic semiconductors for ssDSCs [82]. The conductivity of spiro-OMeTAD is significantly improved by doping using this cobalt(III) complex, see Figure 12. The introduction of the pyrazole moiety, which is a strong π -acceptor, leads to the positive shift in its redox potential, exhibiting redox potential of 1.06 V *vs* NHE. The charge transfer reaction occurred between the redox potential of FK102 and HOMO level of spiro-OMeTAD (0.72 V *vs* NHE), indicating a driving force of 340 mV. Two years later, two new cobalt-based p-type dopants, named tris(2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine)cobalt(III) tris[bis-(trifluoromethylsulfonyl)imide] (FK209) and bis(2,6-di(1*H*-pyrazol-1-yl)pyridine)cobalt(III) tris[bis-

(trifluoromethylsulfonyl)imide)] (FK269), were introduced [83]. The structural modification enables higher solubility of the dopants in organic solvents as well as tunability of their redox potential. Enhanced V_{oc} and FF are observed were attributed to the better solubility due to the counter ions, leading to enhanced charge transfer reaction. The application of FK209 in solid state organic-inorganic lead halide perovskite solar cells achieves 10.4% power conversion efficiency, highlighting the important of chemical doping in improving device performacnes.

Figure 12. (a) IV characteristics of spiro-MeOTAD films spin-cast from $CHCl_3$ solution containing different amounts of FK102 dopant (b) Derived electrical conductivity as a function of doping level [82].

Since the charge transfer reaction greatly depends on the ionization energy level of dopant and HTM, the driving force decides the efficiency of the oxidation reaction. Moreover, the V_{oc} of the devices could be further improved by using HTM with deep HOMO level, therefore, developing new cobalt-based dopants with deep redox potential is extremely important for solution processed high efficiency photovoltaics.

2.6 Organometal halide perovskite solar cells

The term “perovskite” initially referred to calcium titanate ($CaTiO_3$) and later on was used to describe any material with the same crystal structure as $CaTiO_3$. Generally, perovskites possess a chemical formula of ABX_3 where A is a cation, B is a divalent metal ion such as Pb^{2+} or Sn^{2+} and X is an anion (normally a halide I^- , Br^- or Cl^-). The

ideal cubic structure of perovskite forms a three-dimensional network by connecting MX_6 octahedra with small cations occupying the cuboctahedral voids. The cubic structure of a typical ABX_3 perovskite is depicted in Figure 13.

The pioneering work on using organic-inorganic perovskite (methylammonium lead iodide, $\text{CH}_3\text{NH}_3\text{PbI}_3$) as light absorber in a liquid state DSCs showed only 3.8% power conversion efficiency [84]. Its instability in inorganic solvent means that it is not a promising light harvesting material for liquid state DSCs [85]. This material started to attract considerable attention after the work on ssDSCs employing $\text{CH}_3\text{NH}_3\text{PbI}_3$ as light harvester in combination with spiro-OMeTAD as hole transporter and produced over 9% conversion efficiency [86]. The organic-inorganic lead halide perovskite absorbers meet all the criteria as light absorbers for modern photovoltaics such as being solution processable and highly crystalline at low temperature, as well as having excellent perfect materials characteristics [87], *e.g.* high optical absorption [85], long charge diffusion length, low trap density and also efficient charge collection [88-90]. In a very short period, the power conversion efficiency based on this material has increased drastically through a process of optimization of factors such as deposition techniques [91-93], the hole transporter [94, 95], the scaffold and the interfaces [96, 97]. To date, the record efficiency certified by National Renewable Energy Laboratory (NREL in USA) has reached 20.1%.

Figure 13. Typical cubic perovskite structure bearing chemical formula of ABX_3 where A is cation, B is metal ion and X is anion.

There are two main device configurations for perovskite solar cells which are (1) planar devices and (2) mesoscopic devices which are depicted in Figure 14. High efficiency perovskite solar cell can only be obtained in the presence of HTM. Hence, HTM with high conductivity is favourable which could be induced from chemical doping. Therefore, developing of new cobalt dopant is essential in enhancing the overall efficiency, particularly in V_{oc} and FF.

Figure 14. Schematic diagrams of cross-sectional device of planar and mesoscopic devices.

Chapter 3

Experimental Section

3.1 Materials preparation

3.1.1 Synthesis of Co(II/III) redox mediators

Synthesis of tris-(2,2'-bipyridine)cobalt(II) bis(trifluoromethanesulfonimide) [Co(bpy)₃(TFSI)₂]

The synthetic route to the cobalt-based redox complexes was modified from a literature method [46]. Briefly, 1 equivalent (0.5 g) of cobalt(II) chloride hexahydrate (CoCl₂·6H₂O, Sigma Aldrich) was first dissolved in 5 ml of methanol and another methanolic solution (2 ml) of 3.2 equivalents (1.05 g) of 2,2'-bipyridyl (Sigma Aldrich) ligand was added. The solution was stirred at 60 °C for 1 hr. The solution was allowed to cool down to room temperature and a 10-fold excess of lithium bistrifluoromethanesulfonimide (LiTFSI) salt (Sigma Aldrich) was added into the solution. The solution was then stirred at room temperature for 30 min. Deionized water was added to the solution to induce precipitation. The solid formed was collected by filtration and washed successively with water and diethyl ether. The solid was dried under vacuum and used without further purification. The Co(bpy)₃(TFSI)₂ was obtained as a yellowish brown solid.

Co(bpy)₃(PF₆)₂ derivative was synthesized as above by replacing LiTFSI with ammonium hexafluorophosphate (NH₄PF₆).

Synthesis of tris-(2,2'-bipyridine)cobalt(III) tris(trifluoromethanesulfonimide)
[Co(bpy)₃(TFSI)₃]

1 equivalent (0.5 g) of Co(bpy)₃(TFSI)₂ was redissolved in a minimal amount of acetonitrile and an excess (2.5 equivalents, 134 mg) of the oxidizing agent nitrosyl tetrafluoroborate (NOBF₄, Sigma Aldrich) was added to the solution. The solution was stirred at room temperature for 15 min. A 5-fold excess of LiTFSI (0.66 g) was added to the solution which was stirred for another 15 min. Water was added to precipitate the desired product. The solid formed was collected by filtration and washed with water and followed by diethyl ether. The solid was dried under vacuum and used without further purification. The product, Co(bpy)₃(TFSI)₃, was obtained as a light yellow solid.

Co(bpy)₃(PF₆)₃ derivative was synthesized as above by replacing LiTFSI with ammonium hexafluorophosphate (NH₄PF₆).

Synthesis of 2-(1-isopropyl-imidazol-2-yl)pyridine ligand

1 equivalent (4.0 g) of 2-(1*H*-imidazol-2-yl)pyridine (Sigma Aldrich) and 1.5 equivalent (5.72 g) of potassium carbonate (Sigma Aldrich) were both dissolved in dimethylformamide (15 ml) and the solution was stirred at room temperature. The solution was slowly heated up to 100 °C and 1.2 equivalent (3.1 ml) of 2-bromopropane (Sigma Aldrich) was added and the solution was kept stirred at 100 °C for 24 hours. The coupling reaction was monitored by thin layer chromatography. The solution was subsequently cooled down to room temperature. 100 ml of water is added to the solution and extracted 3 times with dichloromethane (30 ml each). The organic phases were combined and dried over MgSO₄ before filtration. The filtered solution was concentrated using a rotary evaporator. The resulting oil was purified using column chromatography with hexane:ethylacetate (1:1) as eluent. The desired compound was obtained as a

yellowish oil. Yield: 68%. ^1H NMR (400 MHz, CDCl_3): δ 8.59 (d, 1H, ArH), 8.17 (d, 1H, ArH), 7.76 (d, 1H, ArH), 7.26 (m, 2H, ArH), 5.95 (m, 1H, ArH).

Synthesis of tris-[2-(1-isopropyl-imidazol-2-yl)pyridine]cobalt(II) bis(hexafluorophosphate)

The desired complex was synthesized according to the synthesis of $\text{Co}(\text{bpy})_3(\text{PF}_6)_2$ mentioned above by replacing the ligand with 2-(1-isopropyl-imidazol-2-yl)pyridine (1.26 g).

Synthesis of tris-[2-(1-isopropyl-imidazol-2-yl)pyridine]cobalt(III) tris(hexafluorophosphate) (MY14)

The desired complex was synthesized according to the synthesis of $\text{Co}(\text{bpy})_3(\text{PF}_6)_3$ mentioned above by replacing the starting material $\text{Co}(\text{bpy})_3(\text{PF}_6)_2$ with tris-[2-(1-isopropyl-imidazol-2-yl)pyridine]cobalt(II) bis(hexafluorophosphate).

3.1.2 Synthesis of dopant for spiro-OMeTAD

Synthesis of 2-(1H-pyrazol-1-yl)pyridine

1 equivalent (4.0 g) of pyrazole (Sigma Aldrich) and 1.2 equivalent (7.91 g) of potassium *tert*-butoxide (Sigma Aldrich) were both dissolved in dimethyl sulfoxide (20 ml) with stirring at room temperature. Upon the complete dissolution, 0.9 equivalent (4.55 ml) of 2-fluoropyridine (Sigma Aldrich) was added into the solution and the solution was slowly heated up to 120°C and stirred for 4 h. The coupling reaction was monitored by thin layer chromatography. The solution was subsequently cooled down to room temperature. 100 ml of water was added and extracted 3 times with

dichloromethane (30 ml each). The organic phases were combined and dried over MgSO_4 before filtration. The filtered solution was concentrated using a rotary evaporator. The resulting oil was purified by column chromatography using dichloromethane as eluent. The desired compound was obtained as an oil which slowly crystallized as white crystals upon standing. Yield: 69%. ^1H NMR (400 MHz, CDCl_3): δ 8.52 (d, 1H, ArH), 8.33 (d, 1H, ArH), 7.94 (d, 1H, ArH), 7.69 (m, 2H, ArH), 7.07 (m, 1H, ArH), 6.44 (t, 1H, ArH).

Synthesis of tris[2-(1H-pyrazol-1-yl)pyridine]cobalt(III) tris(hexafluorophosphate) (FK102)

The synthetic route to this cobalt-based dopant was modified from a literature method [82]. 1 equivalent (0.5 g) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich) was first dissolved in 5 ml of methanol and 3.1 equivalents (0.95 g) of 2-(1H-pyrazol-1-yl)pyridine ligand was added. The solution was stirred at 60 °C for 2 hr. The solution was cooled to room temperature and a 10-fold excess (3.42 g) of NH_4PF_6 (Sigma Aldrich) in aqueous solution (10 ml) was added and the solution was stirred for another 30 min at room temperature. The solution was kept in the refrigerator overnight to induce complete precipitation of the compound. The resulting orange solid was collected by filtration and washed with water, then dried under vacuum. Yield: 94%.

1 equivalent (0.5 g) of the dried tris(2-(1H-pyrazol-1-yl)pyridine)cobalt(II) bis(hexafluorophosphate) was dissolved in a minimal amount of acetonitrile (1.5 ml) and an excess (2 equivalents, 30 mg) oxidizing agent NOBF_4 (Sigma Aldrich) was added to the solution. The solution was stirred at room temperature for 30 min. A 5-fold excess (0.52 g) of NH_4PF_6 in aqueous solution (3 ml) was added and the mixture was stirred for another 30 min. The orange solid (FK102) formed was collected by filtration under reduced pressure and washed thoroughly with water, then dried under vacuum. Yield:

92%. ^1H NMR (400 MHz, acetone- D_6): δ 9.50 (m, 3H, ArH), 8.69 (m, 6H, ArH), 7.98 (m, 9H, ArH), 7.24 (m, 3H, ArH) ppm.

Synthesis of 2-(1H-pyrazol-1-yl)pyrimidine

1 equivalent (4.0 g) of pyrazole (Sigma Aldrich) and 1.2 equivalent (7.91 g) of potassium *tert*-butoxide (Sigma Aldrich) were both dissolved in dimethyl sulfoxide (20 ml). The solution was stirred at room temperature until complete dissolution and 0.9 equivalent (6.06 g) of 2-chloropyrimidine (Sigma Aldrich) was added. The solution was heated at 100 °C for 4 h. The solution was cooled down to room temperature. 100 ml of water was added and extracted 3 times with dichloromethane (30 ml). The organic phases were combined and concentrated using a rotary evaporator. The desired compound was obtained as an oil. Yield: 82%. ^1H NMR (400 MHz, CDCl_3): δ 8.69 (d, 2H, ArH), 8.54 (d, 1H, ArH), 7.78 (d, 1H, ArH), 7.15 (t, 1H, ArH), 6.45 (d, 1H, ArH). ^{13}C NMR (400 MHz, CDCl_3): δ 159.5, 156.6, 144.3, 129.8, 119.3, 109.4.

Synthesis of tris[2-(1H-pyrazol-1-yl)pyrimidine]cobalt(III) tris[bis(trifluoromethylsulfonyl)imide] (MY11)

To a methanolic solution (2 ml) of 3 equivalent (0.92 g) of 2-(1H-pyrazol-1-yl)pyrimidine ligand, 1 equivalent (0.5 g) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich) in 10 ml of methanol was slowly added to avoid polymerization. The solution was stirred at 60 °C for 1 hr. The solution was cooled to room temperature and a 10-fold excess (6.03 g) of LiTFSI (Sigma Aldrich) in aqueous solution (5 ml) was added into the solution and the mixture was stirred for another 30 min at room temperature. The precipitate formed was collected by filtration and washed thoroughly with deionized water, then dried under vacuum. Yield: 94%.

1 equivalent (0.5 g) of the dried tris[2-(1*H*-pyrazol-1-yl)pyrimidine]cobalt(II) bis[bis(trifluoromethylsulfonyl)imide] was dissolved in a minimal amount of acetonitrile (1.5 ml) and an excess (2 equivalents, 0.11 g) of the oxidizing agent NOBF₄ (Sigma Aldrich) was added to the solution. The solution was stirred at room temperature for 30 min. A 5-fold excess (0.68 g) of LiTFSI in aqueous solution (10 ml) was added and the mixture was stirred for another 30 min. The orange solid (MY11) formed was collected by filtration and washed thoroughly with water, then dried under vacuum. Yield: 78%. ¹H NMR (400 MHz, CD₃CN): δ 9.25 (m, 3H, ArH), 9.10 (m, 3H, ArH), 7.91-7.79 (m, 6H, ArH), 7.67-7.59 (m, 3H, ArH), 7.13 (m, 3H, ArH).

3.1.3 Synthesis of methylammonium iodide

Methylammonium iodide was synthesized through a literature procedure. To a round bottom flask containing 9.29 ml of methylamine (40 % in methanol, TCL), 10 ml of hydriodic acid (57 wt% in H₂O, Sigma Aldrich) was slowly added. The flask was kept in an ice bath and the mixture was stirred for 2 hr. The solution was concentrated using a rotary evaporator. The solid formed was washed thoroughly using diethyl ether and recrystallized several times from ether/ethanol until a white solid was obtained. The collected solid was subsequently dried under vacuum at 60 °C and stored in a glove box due to its hygroscopic nature.

3.2 Solar cell fabrication

3.2.1 Preparation of PEDOT counter electrodes

Electropolymerization of poly(3,4-ethylenedioxythiophene), PEDOT, (Figure 15a) on FTO was performed by a modified literature method [98]. The PEDOT counter electrode was prepared by electropolymerization in a three-electrode configuration cell. The working electrode, a cleaned fluorine-doped tin oxide (FTO) substrate, was

immersed into the cell containing 0.01 M of EDOT (Sigma Aldrich) in 0.1 M aqueous sodium dodecyl sulphate (SDS, Sigma Aldrich) solution. Stainless steel grid and a leak-free Ag/AgCl electrode were used as counter and reference electrodes, respectively. The PEDOT film was deposited potentiostatically using a DC potential of 1.2 V for 30 s. The PEDOT counter electrode (see Figure 15b) was subsequently rinsed with deionized water and ethanol. The top-view FESEM image of this PEDOT counter electrode is given in Figure 15c, indicating a rough morphology which provides a high surface area for regenerating the redox couples.

Figure 15. (a) Chemical structure of PEDOT and (b) PEDOT-deposited flourine-doped tin oxide (FTO) glass substrates (c) Top view FESEM image of PEDOT counter electrode deposited on FTO.

3.2.2 Fabrication of conventional DSCs and solid state perovskite solar cells

For liquid electrolyte based DSCs, fluorine-doped tin oxide (FTO) glass substrates (Pilkington, TEC15) were cleaned with Decon90 solution in an ultrasonic bath for 30 min and subsequently rinsed with water and ethanol. Pre-TiCl₄ treatment was conducted by submerging the cleaned FTO substrates in a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min. The TiCl₄ pre-treated substrates were then rinsed with water and ethanol again and dried. Mesoporous TiO₂ films (0.16 cm²) were screen printed using colloidal TiO₂ paste (Dyesol DSL 18 NR-T) and dried at 125 °C between deposition steps. Two layers of scattering TiO₂ layer (Dyesol WER2-O) were deposited on top of the mesoporous TiO₂ film. The electrodes with total thickness of approximately 10 μm were subsequently heated to 500 °C for 15 min with programmed temperature ramping. After sintering, the electrodes were treated again with 40 mM TiCl₄ at 70 °C for another 30 min and rinsed as above. A final heating process was performed at 500 °C for 30 min.

Once cooled, the electrodes were immersed in 0.2 mM sensitizers (D35 from Dyenamo AB, Sweden whereas L102 and C218 was synthesized in our lab) in ethanol for 4 hr. Solar cells were assembled with PEDOT counter electrode using 25 μm thick hot-melt spacer (Surlyn, Dupont). Cobalt electrolyte was injected *via* two predrilled holes at the counter electrode and sealed with Surlyn and a glass coverslip.

Figure 16. Schematic diagram of dye sensitized solar cell with PEDOT counter electrode and Co-complex redox electrolyte.

For devices in Chapter 6, the electrodes were immersed in 0.3 mM of N719 or C106 (both from Dyesol) in acetonitrile:*t*-butanol (1:1) for 16 hours and 0.3 mM of phosphonic acid solution (HPA, DPA or ODPa from Sigma Aldrich) for 4 hours.

For solid state perovskite solar cells, fluorine doped tin oxide (FTO) substrate was first etched using Zn powder and hydrochloric acid (HCl, 4M). The etched FTO was subsequently cleaned using Decon90 solution and ethanol. The substrate was then immersed in 40 mM of TiCl₄ solution at 70 °C for 30 mins. A thin compact TiO₂ layer was deposited by spray-pyrolysis as blocking layer at 450 °C. The solution used for spray-pyrolysis contains titanium diisopropoxide bis(acetylacetonate) (75 wt. % in isopropanol) and absolute ethanol in ratio of 1:9 (by volume). A mesoporous TiO₂ layer was then deposited on the substrate by spin-coating TiO₂ paste and the substrate was calcined at 500 °C for 30 mins. The sintered substrate was again immersed in 40 mM TiCl₄ solution at 70 °C for 30 mins, followed by second sintering at 500 °C for 30 mins.

The light absorber CH₃NH₃PbI₃ perovskite was deposited by using sequential deposition (two-step method) as reported in literature [93]. The schematic diagram of perovskite formation is illustrated in Figure 17. Lead iodide solution (1 M in dimethylformamide, DMF) was initially spin-coated on the substrate at 6000 r.p.m for 5 s, followed by drying at 70 °C for 30 mins. The PbI₂-coated substrate was subsequently immersed into CH₃NH₃I solution (10 mg/mL in 2-propanol) for 20 mins to complete the conversion of PbI₂ into CH₃NH₃PbI₃. Finally, the substrate was rinsed with 2-propanol and dried at 70 °C for 30 mins.

A spiro-OMeTAD solution (100 mg in 1 ml chlorobenzene) containing lithium bis(trifluoromethylsulfonyl)imide (24.21 μL of 520 mgml⁻¹ stock solution), *tert*-butylpyridine (40 μL) and 15.8 mol % of FK102 cobalt dopant (11.98 mg in 39.93 μL MeCN) was spin-coated on top of the perovskite film. Finally, a gold counter electrode

with approximate 100 nm thickness was deposited through a patterned mask using a thermal evaporator.

Figure 17. Schematic diagram of perovskite formation and device architecture.

3.2.3 Composition of electrolytes

All the cobalt based electrolytes were prepared in acetonitrile. The composition of electrolytes for each study are listed below:

For Chapter 4 study:

Cells	1	2	3	4	5	6	7	8
Co(bpy) ₃ (TFSI) ₂ / M	0.10	0.10	0.10	0.10	0.15	0.20	0.15	0.20
Co(bpy) ₃ (TFSI) ₃ / M	0.033	0.033	0.033	0.033	0.05	0.066	0.05	0.066
TBP / M	0.1	0.3	0.4	0.5	0.4	0.4	0.6	0.8
LiTFSI / M	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

For Chapter 5 study:

Electrolyte	E1	E2	E3	E4	E5	E6	E7	E8
Co(bpy) ₃ (TFSI) ₂ / M	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22
Co(bpy) ₃ (TFSI) ₃ / M	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
TBP / M	-	0.2	-	-	0.2	0.2	0.2	0.2
5CB / M	-	-	0.2	-	0.1	0.2	-	-
8CB / M	-	-	-	0.2	-	-	0.1	0.2
LiTFSI / M	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

For Chapter 6 study:

0.22 M of Co(bpy)₃(TFSI)₂, 0.05 M of Co(bpy)₃(TFSI)₃, 0.2 M of TBP and 0.1 M of LiTFSI.

For Chapter 7 study:

Cobalt complexes for each electrolyte:

- Standard electrolyte: tris-(2,2'-bipyridine)cobalt(II) bis(hexafluorophosphate) and tris-(2,2'-bipyridine)cobalt(III) tris(hexafluorophosphate)
- MY14 electrolyte: tris-[2-(1-isopropyl-imidazol-2-yl)pyridine]cobalt(III) bis(hexafluorophosphate) and tris-[2-(1-isopropyl-imidazol-2-yl)pyridine]-cobalt(III) tris(hexafluorophosphate)

Electrolyte	Standard	MY14
Co ^{II} / M	0.22	0.22
Co ^{III} / M	0.05	0.05
TBP / M	0.2	0.2
LiTFSI / M	0.1	0.1

For Chapter 8 study:

The spiro-OMeTAD solution: 100 mg of spiro-OMeTAD in 1 ml of chlorobenzene, 24.21 μL of LiTFSI (520 mgml^{-1} stock solution), 40 μL of *tert*-butylpyridine and 15.8 mol % of FK102 cobalt dopant (11.98 mg in 39.93 μL acetonitrile).

3.3 Characterization techniques

For photovoltaic characterization, the solar cells with an active area of 0.16 cm^2 were measured using a solar simulator (San-EI Electric, XEC-301S) under AM 1.5G standard irradiation with a metal mask of 0.25 cm^2 . For perovskite solar cells, the active area is 0.2 cm^2 . The J - V characteristics were recorded using a Keithley 2612A SourceMeter by applying external potential while measuring the photocurrent response. For light intensity dependence studies, the light intensity was adjusted by using UV Fused Silica Metallic Neutral Density Filters (Newport Corporation) with different transmittance. Incident photon to current efficiency (IPCE) was carried out in DC mode using PVE300 (Bentham) with dual Xenon/quartz halogen lamp as light source. Photocurrent-transient measurement was performed using AutoLab PGSTAT302N under illumination pulse. The pulse lasts 4 seconds for ensuring the steady state was achieved during the pulse. Linear fitting was conducted by the simple linear model, $y = a + bx$, where a is the intercept and b is the slope with confidence level of curve in 95 %.

For electrochemical impedance spectroscopy (EIS), measurements were conducted using AutoLab PGSTAT302N under illumination condition and different bias potentials were applied, ranging from 0.05 V to open-circuit voltage and the frequencies are set between 1 MHz and 0.1 Hz. The I - V measurement provides fundamental information whereby the device performance of the device can be monitored. However, it does not offer evidence for the mechanisms governing the performance. The electrochemical impedance spectroscopy (EIS) allows separation of resistances and capacitances and hence provides detailed information about the electronic processes. Basically, resistance relates to electron transfer or transport while capacitance corresponds to charge carrier accumulation and distribution in the device.

Figure 18.(a) EIS spectrum measured at V_{oc} and (b) complete equivalent circuit model for fitting [31].

The typical impedance spectrum of a DSC measured at V_{oc} is depicted in Figure 18a. The high frequency arc represents charge transfer resistance at counter electrode, R_{CE} , and the interfacial Helmholtz capacitance, C_{pt} . The second arc corresponds to the recombination resistance at TiO_2 /electrolyte interface, R_{rec} , and the chemical capacitance of TiO_2 , C_μ . The third arc is due to the diffusion resistance in electrolyte, R_d . The FTO resistance, R_s , is the initial displacement of the arcs from the origin.

Figure 18b shows the complete transmission line model for fitting the impedance data. The model includes FTO resistance (R_s), transport resistance of electrolyte in TiO_2 film (R_{tr}), interfacial recombination (R_r), capacitance of TiO_2 film (C_μ), the diffusion of electrolyte in porous matrix and in the bulk electrolyte layer between TiO_2 film and counter electrode (Z_d), the charge transfer resistance at counter electrode (R_{CE}) and capacitance of the electrical double layer at the counter electrode (C_{CE}).

Figure 19. (a) recombination resistance and (b) chemical capacitance of DSCs measured under different applied voltage [31].

Typical recombination resistance and chemical capacitance plots of DSCs are shown in Figure 19. For recombination resistance, charge transfer from back layer dominates at low applied voltage and the slope is generally small. At higher applied voltage, charge recombination between electrons from TiO_2 and electrolyte dominates. For the characteristic of chemical capacitance, the dominant capacitance at low applied voltage is the combination of capacitances at counter electrode and the bare conducting substrate surface. At high applied voltage, the dominant capacitance is the chemical capacitance of TiO_2 .

Generally, when comparing the chemical capacitance of two devices, there is a shift observed in chemical capacitance of TiO_2 . The higher the conduction band the larger the displacement of the capacitance. Variations in conduction band will influence the recombination resistance. In order to compare the recombination resistance of two devices, the effect of conduction band position should be removed, thus R_{rec} has to be plotted against common equivalent conduction band, V_{ecb} .

$$V_{ecb} = V_F - \Delta E_c / q$$

where ΔE_c is the shift of conduction band with respect to a reference sample.

Considering a possible internal potential drop in series resistance R_s , the voltage measured at outer contacts is given by

$$V_F = V_{app} - j \times R_s$$

Cyclic voltammetry (CV) was performed in a three-electrode setup where platinum, glassy carbon and aqueous Ag/AgCl electrodes were used as working electrode, counter electrode and reference electrode, respectively. The measured potentials were converted using ferrocene/ferrocenium (Fc/Fc^+) as reference. The sample solutions were prepared in 10 mM with 0.1 M of TBAPF_6 as supporting electrolyte. The scan rate for CV was 100 mV s^{-1} .

For material characterization, ^1H and ^{13}C NMR results were obtained using Bruker DPX spectrometer (400 and 100 MHz, respectively). Optical absorption spectra were obtained using UV-3600 spectrometer. The pore volume and pore size of mesoporous TiO_2 films were measured by using Brunauer-Emmett-Teller (BET) Surface Area Analysis. The porosity was calculated from the fraction of the pore volume over the total bulk volume of mesoporous TiO_2 film. The conductivity of pristine spiro-OMeTAD and its FK102- or MY11-doped films were determined using a MMR technologies variable temperature hall measurement system at ambient condition. 4 square gold electrodes ($1.6 \text{ mm} \times 1.6 \text{ mm}$) were thermally evaporated in square geometry onto the spiro-OMeTAD films.

Chapter 4

Modulating photovoltage in Co(II/III) mediated DSCs by electrolyte additive

Dye-sensitized solar cells (DSCs) are photoelectrochemical cells, in which the conversion efficiency of the device can be optimized by varying each of its internal components. Generally, the major components can be categorized as photoanode, electrolyte, sensitizer and counter electrode. Over the past decade, the iodide/triiodide (I^-/I_3^-) system has remained the most widely researched electrolyte in developing highly efficient DSCs due to its properties of slow recombination and fast dye regeneration [15]. It is well known that electrolyte additives are good candidates to ameliorate the performance of DSCs. The most commonly used electrolyte additive for improving the photovoltage of I^-/I_3^- -mediated DSCs is 4-*tert*-butypyridine (TBP) [99]. It has to be highlighted here that, as shown in previous reports, the ion diffusivity in I^-/I_3^- electrolyte is not affected by the presence of TBP, hence no significant change in the diffusion rate of triiodide ions was observed [100].

Recently, the photovoltage limitation of using I^-/I_3^- electrolyte has been solved by utilizing Co(II/III) redox complexes, which has surprisingly yielded more than 1000 mV [42, 43, 47]. It is also worth noting that the combination of a Co(II/III)-based redox electrolyte together with high performance porphyrin-based photosensitizers has yielded high solar-to-electric power conversion efficiency, so that more than 13% efficiency has been achieved [20]. This achievement is attributed to the tuneable redox potential of cobalt complexes *via* ligand modification which consequently produces high photovoltage in the devices. In Co(II/III)-based redox electrolytes, TBP has been introduced as an electrolyte additive for improving device performance, particularly in

the area of photovoltage. As the molecular charges and sizes of iodide/triiodide and Co-based redox couples are noticeably different, distinct diffusivity of electrolyte and rate of interfacial recombination are observed. Hence, the introduction of TBP in Co(II/III) electrolyte can be expected to produce some differences in the device performance. Therefore, in this chapter, the interfacial recombination as well as mass transport behaviour will be systematically examined through an investigation of the effect of TBP electrolyte additive in Co(II/III) mediated DSCs.

4.1 Photovoltaic characteristics

Figure 20. Chemical structures of (a) cobalt^{II/III} tris(bipyridyl) and (b) D35 photosensitizer.

In investigating the effect of TBP, the choice of sensitizers is important. Addition of TBP as electrolyte additive in ruthenium (Ru)-based DSCs will normally lead to an issue of electron injection due to their comparably low LUMO (lowest unoccupied molecular orbital) energy levels [101, 102]. The choice of triphenylamine-based organic sensitizers (D35) (see Figure 20) with high LUMO energy level in this study eliminates the electron injection problem arising from negative conduction band shift, allowing more precise observation of the role of TBP in Co(II/III)-based redox electrolyte. Awareness of incompatibility between platinum counter electrode and Co(II/III)-based electrolyte encouraged the application of poly(3,4-ethylenedioxythiophene) (PEDOT),

which was electro-polymerized from an environmentally friendly aqueous medium (described in Chapter 3) , as counter electrode to replace the platinum counter electrode, which is frequently used in the I^-/I_3^- redox system [42, 45, 63, 64, 103]. Therefore, the photovoltaic performance of DSCs using different TBP and Co(II/III) concentrations were examined after eliminating all the above potential issues which might lead to any inaccurate conclusions.

The power conversion efficiencies (PCE) of D35-sensitized solar cells in Co(II/III) redox electrolyte with various TBP concentrations are summarized in Table 2. 3 devices have been made for each parameters and a total of 24 devices were fabrication for this study. Photocurrent-voltage (I - V) curves of the representative devices in 0.1 M Co^{2+} electrolyte with different TBP concentrations were plotted in Figure 21(a). For ease of comparison, the ratio of Co(II) to Co(III) species in the electrolyte was fixed at 3:1 where the devices are labelled as cell 1 to 4 in Table 2. As shown in Figure 21(b), a 90 mV enhancement in V_{oc} was observed upon increasing the TBP concentration from 0.1 M to 0.5 M in 0.1 M Co^{2+} electrolyte. More TBP molecules will adsorb onto the TiO_2 surface upon increasing the TBP concentration, which subsequently causes the retardation of the rate of interfacial recombination between the electrons in the conduction band of TiO_2 and the Co(III) species in the electrolyte. The electron lifetime in Co(II/III) electrolyte was also reported to be extended by introducing TBP molecules [41]. On the other hand, the TBP molecules present in the electrolyte could also help in shifting the conduction band edge to a more negative potential, which leads to higher V_{oc} in the devices [99, 104]. The details will be discussed in section 4.3 later.

Figure 21. (a) Photocurrent-voltage (I - V) characteristics under illumination with increasing TBP concentration in 0.1 M Co^{2+} electrolyte (light intensity: 100mWcm^{-2} , AM1.5G). (b) Short-circuit current and open-circuit voltage of DSCs with different TBP concentrations in 0.1 M Co^{2+} electrolyte.

Table 2. J - V characteristics with different TBP concentrations in Co(II/III) electrolyte using PEDOT counter electrode. A total of 24 devices were fabricated and tested.

Cells	1	2	3	4	5	6	7	8
$\text{Co}^{\text{II}} / \text{M}$	0.10	0.10	0.10	0.10	0.15	0.20	0.15	0.20
$\text{Co}^{\text{III}} / \text{M}$	0.033	0.033	0.033	0.033	0.05	0.066	0.05	0.066
TBP / M	0.1	0.3	0.4	0.5	0.4	0.4	0.6	0.8
$J_{sc} / \text{mAcm}^{-2}$	8.04 ± 0.22	7.71 ± 0.18	7.44 ± 0.24	6.94 ± 0.20	8.47 ± 0.26	9.30 ± 0.21	8.30 ± 0.26	9.23 ± 0.19
V_{oc} / V	0.86 ± 0.02	0.91 ± 0.01	0.94 ± 0.01	0.95 ± 0.01	0.93 ± 0.01	0.94 ± 0.01	0.95 ± 0.02	0.88 ± 0.01
FF	0.62 ± 0.01	0.62 ± 0.01	0.62 ± 0.01	0.63 ± 0.01	0.67 ± 0.01	0.66 ± 0.01	0.68 ± 0.01	0.73 ± 0.02
$\eta / \%$	4.26 ± 0.03	4.34 ± 0.02	4.32 ± 0.05	4.15 ± 0.01	5.25 ± 0.07	5.77 ± 0.02	5.36 ± 0.02	5.93 ± 0.22

From cell 1 to cell 4, a gradual trend of decreasing short-circuit current (J_{sc}) upon increasing TBP concentration could be observed. One of the reasons for this observation could be the negative shift in potential of the conduction band of TiO_2 through increasing the TBP concentration. This would consequently lead to a decrease in charge injection efficiency from the photo-excited dye to the TiO_2 conduction band. A similar observation of lower electron injection efficiency upon addition of TBP has been previously reported for Ru-sensitized solar cells using the I^-/I_3^- electrolyte [13, 105]. However, this is unlikely to be the reason in this situation. As discussed earlier, the possibility of reducing charge injection efficiency from increasing TBP concentration has been eliminated by choosing the D35 sensitizer which possesses a high LUMO energy level (-1.37 V vs NHE) [53] as compared to that in N719 Ru-based sensitizer (-0.65 V vs NHE) [106]. In addition, optical absorption for D35-sensitized TiO_2 film treated with 0.1 M and 0.5 M TBP electrolyte solution which is depicted in Figure 22, exhibited no dye desorption. Thus, the decline in J_{sc} from cell 1 to cell 4 is not attributed to any dye desorption in the devices. Another possible explanation for the reduction in J_{sc} upon increasing TBP concentration is the increasing viscosity of the electrolyte solution. This will be discussed in more detail in the following section. Nakade *et al.* have also demonstrated a decrease in J_{sc} upon addition of TBP in another Co-based redox system ($Co(abpn)^{0/1+}$) [41]. However, there are major differences between their redox system and the one used in this study, *i.e.* different ligands are used, leading to the formation of $Co^{0/I}$ and $Co^{II/III}$, and different coordination numbers in the Co complexes.

Figure 22. Absorption spectra of D35 on TiO_2 film after treated with 0.1 M TBP and 0.5 M TBP electrolyte and the inset shows the picture of the photoanodes.

The changes in J_{sc} and V_{oc} of cell 3, 5 and 6 are plotted in Figure 23, whereby the TBP concentration was kept constant at 0.4 M and the Co^{II} concentration was increased from 0.10 M to 0.15 M and 0.20 M (with ratio of Co^{II} and Co^{III} species kept at 3:1). It was realised that the J_{sc} increased as Co^{II} concentration increased. More Co^{II} species present in the electrolyte could improve the dye regeneration and, hence lead to a higher photocurrent density under short circuit condition. As predicted, V_{oc} of those devices are not affected greatly by increasing the Co^{II} concentration in the electrolyte.

Figure 23. Short-circuit current (J_{sc}) and open-circuit voltage (V_{oc}) of DSCs with 0.4 M TBP concentration in various Co^{2+} concentration electrolytes.

Further interpreting the device data from Table 2, there is a small decline in J_{sc} when the TBP concentration was further increased to 0.6 M and 0.8 M, while keeping the Co^{II} concentration at 0.15 M or 0.20 M. The reduction of J_{sc} resulted from higher viscosity in electrolyte, which is due to increasing TBP concentration. This is compensated by higher dye regeneration rate in higher redox electrolyte concentrations. Therefore, this result here is in agreement with the hypothesis, which has been stated previously, that the short-circuit photocurrent density is limited by the regeneration of sensitizers rather than the lower electron injection efficiency from photoexcited sensitizers. Interestingly, 0.6 M of TBP in cell 7 does not change the V_{oc} greatly. However, further increase in TBP concentration to 0.8 M causes the V_{oc} to drop from about 0.95 V to 0.88 V in cell 8. From the impedance spectroscopy measurement which is illustrated in Figure 24, the relatively lower V_{oc} in cell 8 can be rationalized by its slightly lower recombination resistance.

Figure 24. Recombination resistances of cell 6 and cell 8 against V_{ech} .

4.2 Mass transport limitation

The V_{oc} dependence on light intensity for the $\text{Co}^{\text{II/III}}$ redox mediated devices with different TBP concentrations is illustrated in Figure 25a. It was found that V_{oc} increased with light intensity for different TBP concentrations. The slopes for each condition were obtained from linear fitting (details in Chapter 3) and the slopes range from 73 mV/decade to 98 mV/decade. An ideal photodiode displays 59 mV/decade at 300 K in the plot of V_{oc} against the log of the incident intensity, I_o . The deviation from ideal photodiode corresponds to nonlinear recombination kinetics, which could be due to electron transfer *via* surface states, effects of the transfer coefficient for the electron transfer process, and/or shifts in the conduction band under illumination.

Figure 25. Light intensity dependence of (a) the open-circuit voltage and (b-d) the current density under short-circuit conditions for DSC with various TBP concentration in different $\text{Co}^{2+/3+}$ concentrations.

J_{sc} is plotted as a function of light intensity in Figure 25b-d. Generally, mass transport in DSCs can be observed from the linearity in the plot of light intensity dependence of short-circuit photocurrent density [59]. In Figure 25b, it can be noticed that the deviation from linearity becomes more significant as the TBP concentrations were increased from 0.1 M to 0.5 M in 0.1 M Co^{II} electrolyte solution. As mentioned previously, the viscosity of TBP is higher as compared to acetonitrile [107], hence the diffusion of Co^{III} ions towards the counter electrode could be restricted at high TBP concentrations after regenerating the oxidized dyes. In order to prove this claim, the diffusion limiting photocurrents of 0.1 M Co^{II} electrolyte with 0.1 M and 0.5 M TBP concentrations are examined in the PEDOT symmetric cells (Figure 26). The diffusion limiting photocurrent of the $Co^{II/III}$ electrolyte with 0.5 M TBP is relatively lower than that when compared with 0.1 M TBP. It has been previously demonstrated that mass transport in Co-based electrolyte is strongly dependent on porosity and pore size of the mesoporous TiO_2 films [59], however, it may not be the reason for the differences in photocurrent density in this study, as the coated mesoporous TiO_2 films are identical (pore size is 27.32 nm whereas porosity is 0.66). The porosity of TiO_2 nanoparticles was determined from the fraction of its pore volume over the total bulk volume of mesoporous TiO_2 film. From Figure 26, the diffusion limiting photocurrents measured from the symmetrical PEDOT cells are 11 and 14 $mA.cm^{-2}$ for 0.5 M and 0.1 M TBP, respectively. The J_{sc} against light intensity plots depicted in Figure 25b show diffusion limiting currents at about 7-8 $mA.cm^{-2}$, particularly at high TBP concentrations. The differences in diffusion limiting currents from devices are considerably smaller than that obtained from the symmetrical PEDOT cells. This is probably caused by the slower diffusion of Co^{III} ions in the TiO_2 film.

Diffusivity of Co^{III} ions can be estimated from the diffusion limiting photocurrent *via* the following equation [42]:

$$I = \frac{2nFcD}{\delta}$$

where I is limiting photocurrent, n is number of electrons, F is the Faraday constant, c is concentration, D is diffusion coefficient and δ is the distance between the electrodes in the symmetric cell. From Figure 26, taking δ to be 20 μm (measured using digital caliper after assembly of two electrodes), c to be 0.033 M and the I for 0.1 M TBP and 0.5 M TBP to be 14.14 mA cm^{-2} and 10.89 mA cm^{-2} respectively, diffusion coefficients for 0.1 M TBP and 0.5 M TBP are $9.06 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $6.98 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively.

Figure 26. The diffusion limiting currents of 0.1 M Co^{I} electrolyte with 0.1 M and 0.5 M TBP concentrations determined from PEDOT symmetric cells at a scan rate of 10 mV/s. Every 20th data point is marked with a symbol.

The viscosity of the electrolyte can, therefore, be deduced from the Einstein-Stokes equation [108]:

$$D = \frac{K_B T}{6\pi\eta r}$$

where D is the diffusion coefficient of Co^{III} , K_B is the Boltzmann constant, T is the temperature, η is the viscosity of electrolyte and r is the radius of Co^{III} . Taking T to be 298.15 K and r to be 11.15 Å (radius of the $\text{Co}(\text{III})$ complex measured from the crystal structure of $[\text{Co}(\text{bpy})_3]\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ [109], the viscosity of the electrolytes possessing 0.1 M TBP and 0.5 M TBP are 2.16×10^{-2} Pa s and 2.81×10^{-2} Pa s, respectively. The difference in viscosity of both electrolytes could be the reason for the lower J_{sc} in high TBP concentration electrolyte.

Furthermore, the incident photon to current efficiency (IPCE) of the cells employing 0.1 M Co^{II} electrolyte with 0.1 M and 0.5 M TBP is depicted in Figure 27. As the measurement is conducted under low light intensity, the IPCE from both devices do not show a clear difference, which subsequently implies that the lower J_{sc} in cell 4 is caused by the mass transport of Co^{III} ions working under 1 sun condition.

Figure 27. Spectra of IPCE for DSCs employing 0.1M Co^{II} electrolyte with 0.1M and 0.5M TBP concentrations.

According to Figure 25c, the mass transport limitation in the electrolyte with a high TBP concentration can be relieved by increasing the concentration of cobalt redox couples. With 0.4 M TBP concentration, an increase of the Co^{II} concentration from 0.10 M to 0.20 M ameliorates the deviation of linearity in the plot of J_{sc} vs light intensity.

Raising the amount of Co^{II} species in the electrolyte increases the yield of dye regeneration process, which promotes higher J_{sc} in the device. The hypothesis of sufficient dye regeneration through introduction of large amount of Co^{II} species in the electrolyte is again proven by the experimental results in Figure 25d. It should be noted that the use of 0.15 M and 0.20 M Co^{II} in the electrolyte can help in eliminating mass transport limitations in the devices, even at higher TBP concentrations (0.6 M and 0.8 M).

4.3 Reducing interfacial recombination

Generally, a shift in potential of the conduction band of TiO_2 will affect the interfacial recombination resistance (R_{rec}) and consequently change the V_{oc} of the device. Therefore, it is necessary to plot the recombination resistance of different devices against the same equivalent value of conduction band position of TiO_2 . Thus, the capacitances of the devices are shifted until they are overlapping each other by taking the capacitance of one device as a reference. This shift eliminates the effect from various conduction band positions and the newly defined potential is called the common equivalent conduction band potential (V_{ecb}) [31]. Recombination resistances of all the devices were plotted against V_{ecb} for comparison as depicted in Figure 28a-c.

According to Figure 28a, it can be seen that gradually increasing TBP concentration from 0.1 M to 0.5 M in the electrolyte will directly increase the recombination resistance of the device. Since the recombination of electrons in TiO_2 is restricted, the concentration of electrons in the conduction band of the semiconductor is higher, which leads to a higher conduction band position, hence displaying higher V_{oc} in the device with higher TBP concentration in electrolyte. In Figure 28b, the recombination resistance of the devices is shown as the TBP concentration is kept constant at 0.4 M, while the cobalt redox electrolyte concentration is increased to 0.2 M. Although the

redox electrolyte concentration is increased, which directly increases the chance of having interfacial recombination, there is no significant difference in recombination which implies that 0.4 M TBP is sufficient to retard the recombination between electrons in the TiO_2 and the Co^{3+} species in the electrolyte. This observation is also in agreement with the device data, where similar V_{oc} are obtained from these devices. Again, in Figure 28c, higher TBP concentration (> 0.4 M) did not further enhance the recombination resistance of the devices. Therefore, there is an optimum TBP concentration for reducing interfacial recombination and, at the same time, without raising mass transport limitation for the cobalt-based redox mediators.

Figure 29 shows the shift of chemical capacitance by increasing the TBP concentration from 0.1 M to 0.5 M. There is approximately 60 mV shift in potential of conduction band of TiO_2 which contributed to about 67% of photovoltage improvement of the device, which has been shown in previous section. In order to further demonstrate that the presence of TBP in the electrolyte does not disturb the energetics of the redox couples, the cyclic voltammogram of $\text{Co}(\text{bpy})_3(\text{TFSI})_2$ measured in the presence and absence of TBP are depicted in Figure 29b. The redox potential of the cobalt complex is 0.57 V *vs* NHE and it is 0.56 V *vs* NHE in the presence of 0.5 M TBP. The redox potential of the cobalt complex is not varied by the presence of TBP. Thus, the improvement in V_{oc} which is determined is not due to the change in redox potential of the cobalt redox couples.

Figure 28. Comparison of recombination resistance of various cells as described in Table 2, plotted against V_{ecb} .

Figure 29. (a) Chemical capacitance (C_μ) of devices using 0.1 M Co^{2+} electrolyte with 0.1 M TBP and 0.5 M TBP, plotted against V_F . (b) Cyclic voltammogram of $\text{Co}(\text{bpy})_3(\text{TFSI})_2$ with or without the presence of TBP.

4.4 Summary

In this chapter, the interfacial recombination as well as the mass transport behavior are examined through modulating electrolyte additive in cobalt-complex redox electrolyte. Through a series of experiments, the photocurrent density of the device with high TBP concentration in the electrolyte can be restricted by the viscous nature of TBP. Viscosity of the electrolyte is increased by raising the concentration of TBP in the electrolyte which consequently slows down the diffusion of Co^{3+} species in electrolyte. This finding is unique as there is no mass transport limitation observed for the conventional I^-/I_3^- electrolyte.

A 90 mV V_{oc} enhancement of the device was achieved by raising the TBP concentration from 0.1 M to 0.5 M in the Co(II/III) redox electrolyte. This observation can be attributed to two factors: Firstly, TBP molecules tend to adsorb onto the TiO_2 surface and acts as a blocking layer which restricts the interfacial recombination between electrolyte and electrons in semiconductors. Impedance spectroscopy has revealed that higher recombination resistance is observed in the electrolyte with higher TBP concentration. Secondly, the presence of TBP in electrolyte leads to a negative shift in potential of the conduction band of TiO_2 and this contributes approximately 67 % of V_{oc} improvement.

The photocurrent density of the device is gradually decreased by approximately 14%, as the TBP concentration is increased. Generally, one of the possible reasons causing the reduction in photocurrent density could be the reduction in injection efficiency, which originated from the decrease in driving force for electron injection from oxidized sensitizer to conduction band of semiconductor. However, this possibility is eliminated in this study as the chosen sensitizer possesses high HOMO energy level, therefore, there should not be an issue for electron injection. It has been realized that the reduction in photocurrent density in this study is caused by the mass transport limitation which is attributed to the increasing viscosity of the cobalt-complex redox electrolyte with high TBP concentration.

The presence of TBP in Co(II/III) electrolyte reduces the interfacial recombination, however, high TBP concentration could lead to the reduction in solar cell performances due to the mass transport limitation. Therefore alternative materials or solutions should be employed in order to achieve high efficiency solar cells based on cobalt electrolytes. In the following chapter, controlling interfacial recombination using cyanobiphenyl compounds for high V_{oc} solar cells will be discussed.

Chapter 5

Controlling interfacial recombination via adsorption of cyanobiphenyl derivatives

As discussed in the previous section, 4-*tert*-butylpyridine (TBP) was introduced into Co(II/III) redox electrolytes as an additive for enhancing the photovoltage of the photovoltaic devices. TBP tends to upshift the conduction band of the TiO₂ semiconductor, which consequently widens the difference between the conduction band of TiO₂ and the redox potential of electrolyte, leading to a higher V_{oc} . In addition, TBP also significantly restricts the interfacial recombination between the TiO₂ semiconductor and the oxidized redox species, which is generally the main drawback for cobalt based electrolytes. However, in the previous section, it has been shown that the addition of TBP in cobalt-complex redox electrolyte may induce a mass transport limitation arising from the viscous nature of TBP. The main consequence of the mass transport limitation in DSCs is that it causes a lower photocurrent density as the oxidized redox species diffuse more slowly towards the counter electrode after regenerating the photo-oxidized sensitizers. Therefore, for cobalt based electrolytes, it is necessary to find a way to enhance the photovoltage of devices without causing a mass transport limitation.

Recently, liquid crystals (LCs) have been utilized as a replacement for ionic liquids which possess high viscosity in DSCs and retard the physical diffusion of oxidized species of redox mediators in the electrolyte. In 2004, LCs were utilized by Grätzel and co-workers to produce a highly conductive solid I^-/I_3^- electrolyte through doping of a mixture of a solid iodide salt and iodine with LCs [110]. Subsequently, Yanagida and co-workers also reported a highly conductive ionic liquid crystalline electrolyte by the self-assembly of imidazolium cations and ionic LCs (C₁₂MImI/I₂). It

has been shown that this ionic liquid crystalline electrolyte generates a higher photocurrent density and higher light-to-electricity conversion efficiency than the non-ionic liquid analogue, C₁₁MImI/I₂ [111, 112]. The introduction of LCs in polymer gel electrolytes could also improve the conductivity and chain mobility in these electrolytes, which forms an effective transport pathway for redox species [113-115]. However, LCs have not been reported as electrolyte additives for enhancing photovoltaic parameters, particularly the photovoltage of the device.

In this chapter, two cyanobiphenyl based liquid crystalline compounds, 4-cyano-4'-pentylbiphenyl (5CB) and 4-cyano-4'-octylbiphenyl (8CB), were introduced into the cobalt(II/III) redox electrolyte as additives and the interfacial recombination was monitored using electrochemical impedance spectroscopy. The power conversion efficiency of the device with LC-containing Co(II/III) electrolyte was also compared to the control without addition of LC additives.

5.1 Influences of additives on photovoltaics characteristics

The chemical structures of the sensitizer (L102) used in this study and the two cyanobiphenyl compounds, 4-cyano-4'-pentylbiphenyl (5CB) and 4-cyano-4'-octylbiphenyl (8CB), which are utilized as electrolyte additives are shown in Figure 30. The cyanobiphenyl molecules can adsorb onto the TiO₂ surface *via* the free electron lone pair located at the cyano moiety. The conduction band of TiO₂ is hence upshifted by the adsorbed cyanobiphenyl molecules due to their electron donating nature which will subsequently result in higher V_{oc}. Moreover, the long hydrophobic tail at the *para*-position of the cyano group could establish an insulating barrier which restricts the interfacial recombination between electrons in TiO₂ and Co³⁺ in the electrolyte.

Figure 30. Chemical structures of (left) two liquid crystals compounds, 4-cyano-4'-pentylbiphenyl (5CB) and 4-cyano-4'-octylbiphenyl (8CB), and (right) sensitizer L102.

The solar cell devices were fabricated using L102 sensitizer, which was prepared according to the reported procedure [116], and different cobalt-based electrolyte compositions with respect to the different concentrations of TBP, 5CB and 8CB (E1 to E8) were used. The J - V characteristics of the devices are summarized in Table 3. It has to be mentioned that the displayed data is based on the device performances which have been measured 1 day after fabrication. This is due to the slower adsorption rate of 5CB and 8CB onto the bare TiO_2 surfaces as compared to TBP. From Figure 31, it can be noticed that the TiO_2 conduction band position is different after adding 5CB and 8CB, as compared to that obtained using TBP. The conduction band position is further shifted to a similar position to that of TBP and this position does not change after a prolonged period. Therefore, it would be reasonable to compare the device data after eliminating the effects of different rates of adsorption of the different additives.

First, the device performances were compared from E1 to E4 in order to understand the roles of 5CB and 8CB as electrolyte additives. It can be observed that the additives mainly cause changes in the photovoltages. The electrolyte with only TBP additive (E2) shows a V_{oc} of 789 mV whereas the V_{oc} of the TBP-free electrolyte (E1) is only 709 mV. Unexpectedly, devices with E3 and E4, in which TBP was substituted with 5CB and 8CB, show further V_{oc} enhancement to 846 mV and 861 mV, respectively. Using 5CB and 8CB as electrolyte additives improves the V_{oc} by 57 mV and 72 mV as

compared to electrolyte E2. This improvement in V_{oc} is attributed to two main reasons, (1) upshifted conduction band and (2) higher recombination resistance (R_{rec}). V_{oc} is defined as the difference between the Fermi level of the TiO_2 conduction band and the redox potential of the electrolyte. In order to remove the possibility of having negative shift in redox potential of the electrolyte upon adding 5CB or 8CB, the corresponding cyclic voltammogram of the redox electrolyte is given in Figure 32. The redox potential of the electrolyte does not change greatly upon adding 5CB and 8CB. Thus, the increase in V_{oc} does not originate from the shifting in redox potential of the electrolyte. It was also found that addition of different additives in electrolyte does not cause any decrease in J_{sc} which will be discussed in another section later.

Table 3. J - V characteristics of DSCs (measured 1 day after fabrication) using various Co(II/III) electrolyte containing different concentration of TBP, 5CB and 8CB as additives. A total of 24 devices were fabricated and tested.

Electrolyte	E1	E2	E3	E4	E5	E6	E7	E8
TBP (M)	-	0.2	-	-	0.2	0.2	0.2	0.2
5CB (M)	-	-	0.2	-	0.1	0.2	-	-
8CB (M)	-	-	-	0.2	-	-	0.1	0.2
J_{sc} ($mAcm^{-2}$)	9.53 ± 0.18	9.38 ± 0.15	9.30 ± 0.22	9.60 ± 0.13	10.27 ± 0.20	9.68 ± 0.17	10.02 ± 0.12	9.40 ± 0.15
V_{oc} (mV)	709 ± 15	789 ± 12	846 ± 10	861 ± 16	830 ± 14	851 ± 12	831 ± 11	893 ± 15
FF	0.73 ± 0.01	0.74 ± 0.01	0.71 ± 0.01	0.65 ± 0.01	0.73 ± 0.02	0.72 ± 0.01	0.71 ± 0.01	0.71 ± 0.01
η (%)	4.93 ± 0.08	5.48 ± 0.07	5.58 ± 0.01	5.37 ± 0.11	6.22 ± 0.15	5.93 ± 0.10	5.96 ± 0.09	6.01 ± 0.09
J_{sc} linearity	0.09	0.09	0.10	0.10	0.10	0.10	0.10	0.09

Figure 31. Chemical capacitance as a function of corrected potential of the devices using electrolyte E1 to E4. (a) fresh devices (b) 1 day after fabrication.

Figure 32. Cyclic voltammogram of pristine $\text{Co}(\text{bpy})_3(\text{TFSI})_2$ and in the presence of 5CB and 8CB.

After understanding had been gained into the roles of 5CB and 8CB as electrolyte additives, the device performance of the electrolyte combining TBP and these LCs compounds were compared. Photocurrent-voltage (I - V) characteristics of devices using electrolytes E2 and E5-E8 are depicted in Figure 33. Without addition of LCs, the pure TBP containing electrolyte displays an overall power conversion efficiency of 5.48 % with J_{sc} of $9.38 \text{ mA}\cdot\text{cm}^{-2}$, V_{oc} of 789 mV and FF of 0.74. Surprisingly, combining the LCs with TBP in electrolyte gives better power conversion efficiency, which is mainly due to their higher V_{oc} . As compared to E2, addition of 0.1 M of 5CB (E5) and 0.1 M of 8CB (E7) enhances the V_{oc} of the devices by 41 mV and 42 mV, respectively. It was found that further increasing the concentrations of 5CB or 8CB to 0.2 M in the electrolyte improves the V_{oc} of the devices significantly. V_{oc} enhancement of 62 mV and 104 mV for E6 and E8 was observed as compared to E2. Average power conversion efficiency of about 6 % was achieved by combining TBP and LCs additives. Coexistence of 0.2 M TBP and 0.1 M 5CB yields the highest efficiency L102-sensitized solar cell with V_{oc} of 830 mV, J_{sc} of 10.27, FF of 0.73 and overall efficiency of 6.22 %. IPCE of devices employing E2 and E5 are shown in Figure 33 (inset). There is no change in the optical absorption of L102-sensitized device upon adding 5CB into the electrolyte.

Figure 33. Photocurrent-voltage characteristics of devices (after 1 day) under illumination using different electrolyte (light intensity: 100 mW.cm⁻², AM1.5G) and IPCE of devices employing E2 and E5. Every 5th data point is marked with a symbol.

5.2 Electrochemical impedance study on interfacial recombination

As previously mentioned, the addition of TBP and LCs in cobalt-based electrolyte restricts the recombination interface between the electron transporter and electrolyte. Electrochemical impedance measurements were performed in order to investigate the interfacial recombination in the devices with different electrolyte compositions.

As discussed in the previous section, the adsorption rates of TBP and 5CB or 8CB are different, thus the results were collected 1 day after fabrication. The different adsorption rate can be observed by measuring the impedance of the devices right after the fabrication and measuring it again after keeping it for one day. The respective plots of chemical capacitance and recombination resistance as a function of voltage are given in Figure 34. When the electrolyte E2 was used, the chemical capacitance and recombination resistance did not change even when the device was stored overnight. However, it can be clearly seen that for electrolyte E3 and E4, both chemical capacitance

and recombination resistance increased after 24 hours of storage. This observation could be due to slower adsorption of 5CB and 8CB, which are present in the electrolyte E3 and E4 respectively, onto the TiO₂ surface. The result from impedance spectroscopy is in agreement with the device performance. The V_{oc} of the device using E3 and E4 are further enhanced after 1 day of fabrication as was highlighted in the previous section.

The plots of recombination resistance as a function of V_{ecb} of devices using different electrolytes combining TBP and 5CB or 8CB are illustrated in Figure 35. As expected, recombination improved when TBP is introduced into the cobalt-complex based redox electrolyte which has been discussed in the previous chapter. By incorporating different amounts of 5CB and 8CB into the standard electrolyte (E2), the recombination resistance of the device using electrolyte E5 to E8 were significantly improved. It has been shown that the recombination in cobalt-complex redox electrolyte could be two orders of magnitude higher than that in conventional I/I₃⁻ electrolyte [21]. Therefore, the longer molecules of 5CB and 8CB impeded the Co³⁺ species in approaching the TiO₂ surface, subsequently reducing the back reaction. Figure 36 shows the schematic diagram of the TiO₂/electrolyte interface. It was deduced that cyanobiphenyl compounds may adsorb onto the bare TiO₂ surface *via* the lone pair electrons located at the nitrogen atom of -CN group which forms an insulating shield in preventing unwanted back reaction. Cyanobiphenyl compounds could also form molecular packing *via* stronger π - π interactions as compared to TBP molecules. Furthermore, the longer hydrophobic chains in cyanobiphenyl compounds could also keep Co³⁺ species further away from the bare TiO₂ surface which subsequently restrict the TiO₂/electrolyte interfacial recombination.

Figure 34. Conduction band and recombination resistance of fresh cell (solid symbol) and cell after 1 day of storage (open symbol) using E2, E3 and E4. Chemical capacitance (C) and recombination resistance (R_{rec}) are plotted against V_f and V_{ecb} , respectively.

Figure 35. Recombination resistance of a collection of DSCs (after 1 day) using different electrolyte.

Figure 36. Schematic diagram of TiO_2 /electrolyte interface showing TBP and 5CB or 8CB as insulating barrier in preventing back reaction between electron in TiO_2 and Co^{3+} species in cobalt-complex redox electrolyte.

5.3 Mass transport and device stability

For photovoltaic applications, it is also important that the electrolyte additives do not have detrimental effects in the devices. According to Table 3, high efficiency devices are achieved using electrolytes with combinations of TBP and either 5CB or 8CB as additives, mainly due to their improved V_{oc} . In order to investigate the mass transport in the device using different electrolyte compositions, photocurrent densities of the devices under short-circuit condition are measured under different light intensities, which are illustrated in Figure 37. Electrolytes consisting of TBP and cyanobiphenyl additives displays linear behaviour (slope is given in Table 3) and there is no limiting photocurrent density at higher light intensity. Therefore, no mass transport limitation was found by adding 5CB or 8CB additive into the standard electrolyte (E2). The result is encouraging as the V_{oc} of the device was enhanced using a combination of TBP and cyanobiphenyl compounds while no reduction in photocurrent was observed.

Figure 37. Light intensity dependence of the current density under short-circuit conditions for DSCs (after 1 day) with various Co(II/III) electrolyte.

Table 4. Charge transfer resistance of DSCs measured at open-circuit potential using different Co(II/III) electrolytes.

Electrolyte	E1	E2	E3	E4	E5	E6	E7	E8
R_{CE} (Ωcm^{-2})	1.38	1.89	1.19	1.15	1.19	1.56	2.29	1.42

Another potential detrimental effect of adding additives into the electrolyte is increasing charge transfer resistance at the counter electrode (R_{CE}). Therefore, R_{CE} of the devices were examined by electrochemical impedance spectroscopy (EIS). The EIS spectra of the devices employing TBP, 5CB and 8CB as electrolyte additives are shown in Figure 38(a) and the R_{CE} of all devices are summarized in Table 4. All the devices exhibit small R_{CE} values (approximately $1\text{--}2\ \Omega\text{cm}^2$), which are considered low for cobalt-complex based redox electrolyte [42]. The device employing electrolyte E8 was chosen as the representative cell in order to test the chemical stability of the device. The cell was stored in dark and tested periodically under 1 sun illumination. The results are shown in Figure 38(b). The results suggest that the addition of cyanobiphenyl compounds as electrolyte additive does not disturb the chemical stability, *e.g.* dye desorption, additive adsorption on counter electrode, degradation of redox mediators, etc.

Figure 38. (a) EIS spectra of devices using E2, E3 and E4 electrolytes measured under illumination at V_{oc} . Symbols represent experimental data and solid lines show the fittings. (b) Stability testing (stored in dark) of DSCs with E8 electrolyte.

5.4 Summary

In this chapter, interfacial recombination was controlled using cyanobiphenyl organic additives and interesting properties were found. The roles of two cyanobiphenyl compounds, 5CB and 8CB, in cobalt-based redox electrolyte were examined. These compounds have been successfully demonstrated as good candidates for electrolyte additives in the cobalt(II/III) redox electrolyte system. It has been found that these additives confer photovoltage improvement from two perspectives, (1) upshifting of the conduction band of TiO_2 and (2) reduction of TiO_2 /electrolyte interfacial recombination.

The best efficiency for a L102-sensitized solar cell was achieved by using a combined electrolyte additives of TBP and 5CB, yielding an overall efficiency of 6.22 %, J_{sc} of 10.27 mA.cm^{-2} , V_{oc} of 830 mV and FF of 0.73. It was also revealed that by utilizing the cyanobiphenyl compound with a longer hydrophobic tail (8CB), a 13.2 % improvement (from 789 mV $\rightarrow$ 893 mV) in V_{oc} can be achieved compared to the device using the electrolyte containing only TBP. The higher V_{oc} is confirmed using EIS in which higher recombination resistance is observed for the device using electrolyte with cyanobiphenyl compound as additive. Meanwhile, slower adsorption of 5CB and 8CB onto the TiO_2 surface is also observed through EIS measurement.

The longer molecular structures of 5CB and 8CB compared to TBP restrict the contact between TiO_2 and redox electrolyte which consequently reduces the interfacial recombination. In the previous chapter, it has been demonstrated that the pure TBP containing electrolyte may exhibit mass transport limitation, particularly at higher concentrations. However, addition of these cyanobiphenyl compounds as additives does not cause any diffusion limitation and it promotes the overall efficiency by guaranteeing a higher V_{oc} . In addition, incorporation of these compounds in the electrolyte does not increase the charge transfer resistance nor disturb the chemical stability of the devices.

The encouraging finding of utilizing cyanobiphenyl compounds as electrolyte additive offers a way for achieving high efficiency solar cells by using cobalt-based redox mediator. After the study of using electrolyte additive in preventing interfacial recombination, it has been realized that the interface between the charge transport layer and electrolyte is crucial in producing high efficiency solar cells. Thus, this provided the motivation for investigating the surface passivation of the charge transport layer for cobalt-complex redox electrolyte, which will be discussed in the following chapter.

Chapter 6

Enhancing recombination resistance and charge collection efficiency through surface passivation

DSCs are photoelectrochemical devices whereby oxidized photosensitizers are reduced to their neutral state by an electrolyte consisting of redox mediators. Upon illumination, the injected electron from photo-excited sensitizers move through the nanocrystalline TiO_2 particles by a trapping/detrapping model and is collected by the conducting substrate before it recombines with the photo-excited sensitizers or oxidized species in the electrolyte [117]. Generally, interaction between the electrolyte and nanocrystalline TiO_2 is detrimental to the device mainly through reduction of V_{oc} of the device from the recombination of electrons in TiO_2 and redox couples [118-120].

Surface coating is one of the direct methods to reduce the TiO_2 /electrolyte interfacial recombination in DSCs. This surface engineering could be beneficial by decreasing the surface trap states of TiO_2 [68], facilitating charge transport [121], improving charge separation efficiency [67] and most importantly, retarding the undesired recombination between photo-excited electrons in the TiO_2 and oxidized species in the electrolyte [65]. The conclusion from the previous two chapters has pointed out the importance of surface passivation of nanocrystalline TiO_2 in DSCs for achieving high efficiency photovoltaic devices. Some research effort has been put into the surface passivation of TiO_2 in DSCs for enhancing the device efficiency, such as depositing a thin layer of metal oxide (e.g. Al_2O_3 , Nb_2O_5 and ZrO_2) [65, 70, 71, 122] or coating an ultrathin layer of insulation by atomic layer deposition [44, 123]. However, a thick or inhomogeneous metal oxide layer could hinder the electron injection from photo-excited sensitizer and ultimately decrease the efficiency of the devices.

Thus, in this chapter, alkanephosphonic acids were introduced as a co-adsorber to passivate the surface of TiO_2 after realizing the high recombination in DSCs using cobalt-complex redox electrolyte. The effect of different chain lengths of alkanephosphonic acids on recombination resistance was examined and the reason for the improved device efficiency was revealed through analysing the charge collection efficiency.

6.1 Solvent-dependent passivation

The chemical structures of the photosensitizer and the co-adsorbers used in this study are given in Figure 39. The effect of surface passivation can be easily highlighted using the N719 sensitizer as high recombination exists between N719 and the cobalt-based electrolyte as seen in earlier reports [52, 54].

Figure 39. Chemical structures of N719 sensitizer and coadsorbers (HPA, DPA and ODPA).

In the study of the solvent effect in surface passivation, DPA is used due to its good solubility in organic solvents and moderately long molecular length, which provides a barrier between TiO_2 electrode and the cobalt-based redox electrolyte. The freshly prepared the TiO_2 film deposited on the conducting FTO substrate was first dipped into the dye bath containing 0.3 mM of N719 for 16 hours to ensure complete adsorption of the sensitizer on the nanocrystalline TiO_2 film. Subsequently, the electrode

was dipped into a different organic solvent systems containing 1 mM DPA for 1 hour, which ensures the bare TiO₂ surface is passivated by phosphonic acid. For the control devices, the N719-sensitized electrode was dipped into the respective solvent (no phosphonic acid) for the same duration. The photovoltaic parameters of the devices are summarized in Table 5 and the respective *I-V* curves are depicted in Figure 40.

Table 5. *I-V* characteristics of N719-sensitized devices with cobalt-based redox electrolyte. The TiO₂ photoanode is treated with DPA in different solvents for 1 hour. The ratio of hexane:ethanol is 9:1. A total of 18 devices were fabricated and tested.

Solvent	Ethanol		Hex:EtOH		EA	
DPA treated TiO ₂	No	Yes	No	Yes	No	Yes
J _{sc} (mA.cm ⁻²)	3.71 ± 0.21	5.19 ± 0.15	2.49 ± 0.16	3.55 ± 0.13	3.04 ± 0.15	3.58 ± 0.14
V _{oc} (mV)	641 ± 10	672 ± 8	626 ± 11	648 ± 10	607 ± 11	625 ± 9
FF	0.62 ± 0.01	0.73 ± 0.02	0.68 ± 0.01	0.77 ± 0.02	0.60 ± 0.01	0.72 ± 0.02
η (%)	1.47 ± 0.04	2.54 ± 0.03	1.05 ± 0.03	1.77 ± 0.01	1.10 ± 0.02	1.61 ± 0.01

The experiment was conducted in three different solvents: ethanol, a mixture of hexane and ethanol (9:1), and ethylacetate. These solvents are used as they would not cause desorption of N719 from the TiO₂ surface. For the hexane:ethanol and ethylacetate solvents, the efficiency for control devices is about 1% which improved to 1.8% and 1.6% after passivation using DPA. The control device in the ethanol system exhibits 1.4% efficiency with a photocurrent density of 3.71 mA.cm⁻², V_{oc} of 641 mV and FF of 0.62. This is close to the reported efficiency for the N719-sensitized device using a cobalt-based redox electrolyte [54]. When the TiO₂ film was treated with DPA ethanolic solution after the dye adsorption, the device displayed improvement in all photovoltaic parameters. The J_{sc} of the device significantly increased to 5.19 mA cm⁻² which represents an almost 40% improvement in photocurrent. The photovoltage of the device was also enhanced as well as the fill factor. The V_{oc} increased to 31 mV and the FF improved to 0.11. Among all these solvents, ethanol is most appropriate for DPA as approximate 2.5% power conversion efficiency has achieved for the DPA treated device.

Therefore, it has been shown that the passivation of TiO_2 using DPA is solvent dependent; it mostly depends on the solubility of DPA in each solvent.

Figure 40. (a-c) Photocurrent-voltage characteristics of N719-sensitized devices in which the mesoporous TiO_2 films are treated with DPA in different solvent system (light intensity: 100 mW.cm^{-2} , AM1.5G). (d-f) IPCE of the respective devices. Every 5th data point is marked with a symbol.

Figure 40d-f shows the IPCE results of the respective devices. The adsorption of DPA onto TiO_2 surface does not alter the absorption onset of the device. However, it can be clearly noticed that the IPCE for the devices with DPA-treated photoanodes was higher as compared to those without DPA-treated photoanode. Generally, the IPCE can

be defined as the product of the light harvesting efficiency (η_{LHE}), collection efficiency (η_{coll}) and injection efficiency (η_{inj}). The equation is given as below [28]:

$$IPCE = \eta_{LHE} \times \eta_{coll} \times \eta_{inj}$$

Since the same sensitizer (N719) is used for all the devices, light harvesting efficiency must be equivalent in all devices. As the injection efficiency depends on the energy level of the sensitizer and TiO_2 , it should also be the same in all devices. Thus, the only parameter in justifying the IPCE is the collection efficiency.

In order to compare the charge collection efficiency, electrochemical impedance spectroscopy is conducted to determine the transport resistance and recombination resistance and the charge collection efficiency can be evaluated by the following equation [124, 125]:

$$\eta_{coll} = 1 / (1 + \frac{R_t}{R_{rec}})$$

The recombination resistance, charge transport resistance and charge collection efficiency of the devices with and without DPA-treated TiO_2 are illustrated in Figure 41. Upon passivating the bare TiO_2 surface with DPA after dye adsorption, the recombination resistance is greatly enhanced, however the charge transport resistance is approximately the same. This shows that having the DPA grafted onto the TiO_2 surface does not affect the electron transport in the device. By calculating the charge collection using the equation mentioned above, it can be easily observed that the charge collection in the DPA-treated device is superior as compared to that without DPA passivation. The charge collection efficiency is kept at almost 100%, when swept up to 0.5 V, which is close to its V_{oc} . This improved charge collection in the DPA-treated device ensures higher IPCE which translates into higher J_{sc} for the device and is in agreement with the device data.

Figure 41. (a) Recombination resistance, (b) transport resistance and (c) charge collection efficiency of the devices with and without DPA-treated TiO_2 in ethanol.

6.2 Chain length effect in preventing back reaction

From molecular dynamics simulations, it has been revealed that the cobalt electrolyte can form a complex with the attached N719, which shortens the distance between the oxidized species of the electrolyte and the TiO_2 surface. This increases the possibility of interaction and thus of recombination between the injected electrons and the oxidized species of the redox electrolyte in the device. Therefore, it is beneficial to keep Co^{3+} further away from the TiO_2 surface for high efficiency solar cells. In the previous section, it has been shown that passivating the bare TiO_2 surface with alkanephosphonic acid could hinder interfacial recombination. Thus, it would be

interesting to investigate the effect of chain length of the alkanephosphonic acid in restricting unwanted back reactions.

Three alkanephosphonic acids, hexyl-, decyl- and octadecylphosphonic acid (depicted in Figure 39), with different chain lengths were grafted onto the bare TiO₂ surface after dye adsorption. Although it has been shown in the previous section that ethanol is a good solvent for preparing DPA solution, a mixture of solvent (hexane:ethanol = 9:1) was used for the alkanephosphonic acid solutions due to the solubility issue for the longer phosphonic acids. Similarly, the N719-sensitized mesoporous TiO₂ films were immersed into 1 mM phosphonic acid solution for 1 hour. The photovoltaic parameters of the devices fabricated using these photoanodes are summarized in Table 6 and the *I-V* curves of these devices are displayed in Figure 42.

Table 6. *I-V* characteristics of N719-sensitized devices with three different phosphonic acids grafted on mesoporous TiO₂. The ratio of solvent is hexane:ethanol is 9:1. A total of 12 devices were fabricated and tested.

	Hex:EtOH	HPA	DPA	ODPA
J _{sc} (mA.cm ⁻²)	2.45 ± 0.16	3.58 ± 0.12	3.74 ± 0.13	3.78 ± 0.14
V _{oc} (mV)	637 ± 14	657 ± 11	666 ± 10	687 ± 12
FF	0.58 ± 0.02	0.73 ± 0.01	0.75 ± 0.01	0.75 ± 0.01
η (%)	0.91 ± 0.07	1.71 ± 0.01	1.87 ± 0.10	1.95 ± 0.06

As expected, the control device displays low efficiency due to the incompatibility of the N719 sensitizer and cobalt-based redox electrolyte. Upon grafting phosphonic acid onto the bare TiO₂ surface, the efficiency of the device is improved. As the alkyl chain length of the phosphonic acid used is increased from 6-carbon to 10-carbon and then 18-carbon atoms, the photocurrent density of the device is increasingly enhanced by 46%, 53% and 54%, respectively. For V_{oc}, the device gained 20 mV, 29 mV and 50 mV as successively longer phosphonic acids were incorporated. The fill factor of the devices are also better as compared to those without phosphonic acid treated device and a fill factor of over 0.7 can be achieved.

Figure 42. (a) Photocurrent-voltage characteristics of N719-sensitized devices in which the mesoporous TiO₂ films are treated with three different alkanephosphonic acids (light intensity: 100 mWcm⁻², AM1.5G). (b) Dark current of the devices.

The presence of dark current of the device is mainly attributed to the loss of the photoinjected electron in the mesoporous TiO₂ and oxidized species (I₃⁻ or Co³⁺) in redox electrolyte. The recombination between the photoinjected electrons and oxidized sensitizers is always negligible as the regeneration of sensitizers is significantly faster than this unfavourable back reaction [28, 126]. To optimize the performance of solar cells, it is important to prevent the recapture of electrons by the oxidized species in electrolyte. Reduction of dark current can generally improve the V_{oc} of the device and can be deduced from the equation below [31]:

$$V_{oc} = \frac{k_B T}{q} \ln \left(\frac{I_{inj}}{I_{dark}} + 1 \right)$$

where k_B is the Boltzmann constant, T is absolute temperature of the device, q is the magnitude of the electron charge, I_{inj} is the injected electron and I_{dark} is the dark current. Thus, in order to obtain higher V_{oc} from the device, it is necessary to reduce the dark current in the device. The comparison of dark current of the devices with and without phosphonic acid treated photoanode is illustrated in Figure 42(b). The onset of dark current of the control device was at 0.1 V which was shifted to about 0.4 V for the phosphonic acid treated devices. The grafted phosphonic acids function as an insulating

barrier which effectively restricts the undesired interfacial recombination, yielding better photovoltaic performance.

Figure 43. (a) IPCE of the devices with and without phosphonic acid treated photoanodes. (b and c) Capacitance and recombination resistance of the devices measured using electrochemical impedance spectroscopy.

The IPCE, chemical capacitance and recombination resistance of those devices are shown in Figure 43. The enhanced IPCE spectra for the devices with phosphonic acid treated photoanodes are attributed to the better charge collection efficiency, as highlighted in the previous section. It was found that the longer phosphonic acid offers better prevention of recombination, hence displaying higher efficiency. The interfacial recombination was investigated using impedance spectroscopy, in which higher recombination resistance was found in the phosphonic acid treated device. Surprisingly, the recombination resistance in these devices was up to one order of magnitude higher than in the control device.

6.3 Influence of photosensitizers

In earlier reports, it has been highlighted that introducing sterically bulky groups onto the redox couples could help in avoiding recapture of electrons in the TiO_2 by Co^{3+} species in the electrolyte [19]. However, the presence of bulky substituents in redox mediators significantly reduces the charge transport and limits the overall performances of the device [39, 55, 57]. It has also been shown that the electron life time is different when different sensitizers (N719 vs Z907) are combined with cobalt-based redox electrolyte [54]. Therefore, the effect of grafting the phosphonic acid onto TiO_2 surface can be different if a different photosensitizer is chosen.

Figure 44. Chemical structures of C106 sensitizer.

The chemical structure of another ruthenium-based sensitizer, C106, is given in Figure 44. It was designed as a high efficient sensitizer and an overall efficiency of over 11% was achieved using I^-/I_3^- electrolyte [127]. It has a pair of long alkyl chains attached to the bipyridyl ligand which could offer a hindrance effect for cobalt-based redox electrolyte. Thus, a comparison between sensitizer N719 and C106 using DPA-treated mesoporous TiO_2 electrodes are summarized in Table 7 and the I - V curves are shown in Figure 45.

Table 7. *I-V* characteristics of N719 and C106 sensitized devices with and without DPA-treated mesoporous TiO₂. A total of 12 devices were fabricated and tested.

	N719		C106	
	Ethanol	DPA	Ethanol	DPA
J _{sc} (mA.cm ⁻²)	3.71 ± 0.15	5.19 ± 0.12	8.64 ± 0.18	9.72 ± 0.17
V _{oc} (mV)	641 ± 14	672 ± 10	702 ± 13	723 ± 12
FF	0.62 ± 0.01	0.73 ± 0.01	0.69 ± 0.01	0.74 ± 0.01
η (%)	1.47 ± 0.01	2.54 ± 0.01	4.18 ± 0.05	5.20 ± 0.07

The control device of C106 displays an overall power conversion efficiency of 4.18%, showing J_{sc} of 8.64 mA.cm⁻², V_{oc} of 702 mV and fill factor of 0.69. Xiang *et. al.* have reported a similar efficiency by combining C106 and aqueous based cobalt electrolyte [128]. When the DPA-treated mesoporous TiO₂ electrode is introduced to the device, the overall efficiency is significantly improved to 5.2%. Every photovoltaic parameter is improved, mainly due to the consistently improved photocurrent. From the dark current shown in Figure 45, the onset is shifted from 0.4 V to 0.5 V, which is a relatively smaller shift, as compared to N719 devices. This was probably due to the presence of the pair of long alkyl chains in the C106 sensitizer. Although the molecular structure of the sensitizer could offer a certain extent of steric hindrance to protect the bare TiO₂ surface from exposure to Co³⁺ ions, a complete passivation using phosphonic acid is crucial to achieve high efficiency solar cells.

Figure 45. (a) Photocurrent-voltage characteristics and dark currents of (a) N719- and (b) C106-sensitized devices using DPA-treated TiO₂ electrodes and their control devices. (light intensity: 100mWcm⁻², AM1.5G).

The IPCE spectra of both N719- and C106-sensitized devices are shown in Figure 46. Similarly, higher IPCE was attributed to better charge collection efficiency due to higher recombination resistance of DPA-treated devices. The impedance results of C106 devices are shown in Figure 47. From the plots of chemical capacitance versus voltage, it can be deduced that the conduction band edge lies at similar energy levels for both control devices and DPA-treated devices. This implies that there is no significant shift in conduction band edge upon grafting the DPA onto TiO_2 surface. The recombination is also enhanced upon TiO_2 passivation using DPA. This is in agreement with the observation for N719 device previously.

Figure 46. IPCE of (a) N719- and (b) C106-sensitized devices using DPA-treated TiO_2 electrodes and their control devices.

Figure 47. Chemical capacitance and recombination resistance of (a,b) N719- and (c,d) C106-sensitized devices.

6.2 Summary

In this chapter, the effect of grafting phosphonic acid onto the TiO₂ surface after dye adsorption in DSCs using cobalt-based redox electrolyte was discussed based on its recombination resistance and charge collection efficiency. Alkanephosphonic acid was demonstrated as a potential surface adsorber for passivating the TiO₂ surface which helps to avoid undesired recapture of electrons in TiO₂ by Co³⁺ species in cobalt-based redox electrolyte.

The alkanephosphonic acid treated TiO₂ electrode improved all photovoltaic parameters of the device mainly by (1) providing better charge collection and (2) reducing interfacial recombination. The enhancement in photocurrent density, which has been proven in IPCE measurements, is attributed to the better charge collection efficiency in phosphonic acid grafted devices. Other than J_{sc}, the V_{oc} of the device was also improved as well as its fill factor. Results derived from impedance spectroscopy have shown that the recombination resistance of the device is significantly enhanced due to the blocking effect from attached phosphonic acid on the TiO₂ surface, where electrons do not easily recombine after injection into the conduction band of TiO₂. It was also found that the dark current of the device has also positively shifted by about 100 - 200 mV as compared to the control device, depending on the type of sensitizers used. Depending upon solvent efficiency improvements of between 45% and 78% were obtained, which are better than the 35% improvement obtained using metal oxide layers on TiO₂.

Structural modification may incorporate long alkyl chains into the molecular structures of sensitizer, however, in this chapter, it has been shown that it is still insufficient for the prevention of interfacial recombination existing within the cobalt(II/III) redox mediated DSCs, especially those sensitized with ruthenium-based

light absorber. However, TiO_2 passivation using alkanephosphonic acids could greatly enhance the photovoltaic performances by reducing exposure of the bare TiO_2 surface from exposure to the electrolyte.

After understanding the importance of TiO_2 passivation in devices using cobalt-based electrolyte, in the following chapter, the structural engineering of cobalt redox couples in reducing unfavourable back reaction which could lead to higher V_{oc} of DSCs will be demonstrated.

Chapter 7

Hindering electron recapture through structural modification of cobalt redox mediators

Reducing interfacial recombination between photoinjected electrons and the oxidized species of redox mediators is crucial for cobalt electrolyte mediated DSCs, so as to achieve high efficiency devices. Severe interfacial recombination could have detrimental effects on photovoltaic parameters, especially by lowering the V_{oc} of the devices. In the previous chapters, it has been demonstrated that the photovoltage of the device can be modulated by varying the electrolyte composition, introducing electrolyte additives and passivating the surface of the electron transport layer.

Another feasible way of restricting the interfacial recombination is by modifying the chemical structure of the cobalt complex. Owing to its slow transfer kinetics and the cationic nature of the cobalt complexes, cobalt-based electrolytes may experience a recombination rate two orders of magnitude higher than the conventional I^-/I_3^- electrolyte [21, 41, 129]. The most widely used cobalt complex as a redox mediator is tris(bipyridyl) cobalt based complex, in which more than 13% efficiency has been achieved [20]. Incorporating a bulky group to the ligand of cobalt complexes was found to improve the electron lifetime of the device, however the bulkiness of the ligands also hinders the diffusion of the redox mediators, as reflected in the lower photocurrent density of the device [46].

There are not many alkyl bipyridyl derivatives that have been used in synthesizing cobalt redox mediators. The alkyl bipyridyl derivatives most commonly used in producing cobalt redox couples are dimethyl and di-*tert*-butyl pyridine ligands [46, 57, 130]. One of the main drawbacks of modifying the bipyridyl ligand is its multi-

step synthesis with a relatively low yield of the desired products. In this chapter, an alkyl imidazolylpyridine ligand was used to synthesize the cobalt redox couples and the effects on structural modification to the device performances will be discussed and compared to conventional cobalt-based electrolyte, which is depicted in Figure 49(a).

7.1 Design and synthesis of cobalt(II/III) redox mediator

The alkylation of bipyridine requires a multistep synthesis, which has a relatively low yield. 2-(1*H*-Imidazol-2-yl)pyridine is a similar ligand to the bipyridyl ligand, as both are bidentate ligands and coordinate to the cobalt metal ion through the nitrogen atoms. The amine group located at the imidazole moiety allows alkylation to occur through a single step synthesis. The synthetic routes to 2-(1-isopropyl-imidazol-2-yl)pyridine ligand (**py-Im-Y**) and the cobalt redox couple are summarized in Figure 48.

Figure 48. Synthetic routes of 2-(1-isopropyl-imidazol-2-yl)pyridine ligand (**py-Im-Y**) and cobalt redox couple (**MY14**).

There is an advantage of using 2-(1*H*-imidazol-2-yl)pyridine as the amine portion in that imidazole moiety can be easily deprotonated in mild basic condition using potassium carbonate. Once the amine group is deprotonated, it becomes nucleophilic and undergoes a $\text{S}_{\text{N}}2$ reaction with the isopropyl bromide, forming the desired ligand, **py-Im-Y**. Upon mixing with stoichiometric amounts of cobalt precursors in methanol solution,

precipitation using ammonium hexafluorophosphate yields the cobalt redox couple, MY14. The chemical structure of MY14 is given in Figure 49.

Figure 49. Chemical structures of (a) Co(bpy)₃(PF₆)₂, (b) MY14 and (c) C218 sensitizer.

7.2 Photovoltaic characteristics

As a redox electrolyte, it is important that the electrolyte solution does not absorb much of the incident visible light. A comparison between the absorption of a typical cobalt electrolyte and iodide/triiodide electrolytes has been shown in Figure 8. The optical absorption spectra of cobalt(II/III) redox shuttles are illustrated in Figure 50. The molar absorptivity of MY14 is as low as the typical Co^{2+/3+}(bpy)₃ electrolyte, which means that the incoming light will not be greatly absorbed by the electrolyte before it reaches the photosensitizers. The inset shows the colour of these cobalt-based redox electrolytes.

Figure 50. Optical absorption spectra of cobalt(II/III) redox couples in electrolyte. Inset shows the colour of the two electrolyte solutions.

The redox potential of this newly synthesized redox couple was examined *via* cyclic voltammetry. The cyclic voltammograms of MY14 and $\text{Co(bpy)}_3(\text{PF}_6)_2$ are displayed in Figure 51. The potential is calibrated using Fc/Fc^+ as standard. The redox potential of $\text{Co(bpy)}_3(\text{PF}_6)_2$ was found to be 0.56 V *vs* NHE, which is in agreement with the reported value [19, 131]. However, the CV curve of MY14 is negatively shifted in potential as compared to $\text{Co(bpy)}_3(\text{PF}_6)_2$ and the redox potential was found to be 0.41 V *vs* NHE. The shift in redox potential is attributed to the weaker electron withdrawing ability of the py-Im-Y ligand as compared to the bipyridyl ligand. It has been shown that introduction of the electron withdrawing groups/atoms to the ligands can tune the redox potential of cobalt complexes positively [47]. The isopropyl group is a weak electron donating group. Therefore, the alkylation of 2-(1*H*-imidazol-2-yl)pyridine reduces the electron withdrawing ability of the ligand and consequently shifts the redox potential of the cobalt complex in the negative direction. It can be estimated that each of the isopropyl group contributes ~ 50 mV shift to its redox potential. Figure 51(b) shows the energy diagram of C218-sensitized DSCs with MY14 or $\text{Co(bpy)}_3(\text{PF}_6)_2$ as electrolyte. It was realized that there is a 150 mV difference in redox potential between the two redox couples, which could limit the photovoltaic performances of the MY14-mediated DSCs.

Figure 51. (a) Cyclic voltammograms of $\text{Co(bpy)}_3(\text{PF}_6)_2$ and MY14. (b) Schematic energy diagram of C218-sensitized DSCs using MY14 and $\text{Co(bpy)}_3(\text{PF}_6)_2$ as electrolyte.

The newly synthesized MY14 and $\text{Co(bpy)}_3(\text{PF}_6)_2$ was further oxidized using NOBF_4 and the electrolyte solutions were prepared accordingly: 0.22 M of MY14 or $\text{Co(bpy)}_3(\text{PF}_6)_2$, 0.05 M of MY14^+ or $\text{Co(bpy)}_3(\text{PF}_6)_3$, 0.1 M LiTFSI and 0.2 M of TBP. The photocurrent-voltage characteristics of C218-sensitized device are shown in Figure 52(a). It can be seen that both devices possess approximately $12 \text{ mA}\cdot\text{cm}^{-2}$ photocurrent densities under 1 sun illumination. It is known that IPCE is a product of light harvesting efficiency (η_{LHE}), injection efficiency (η_{inj}), charge collection efficiency (η_{coll}) and regeneration efficiency (η_{reg}). Since the same sensitizer is used in both devices, the light harvesting efficiency should be the same in both devices. According to the IPCE spectra of both devices, which are depicted in Figure 52(b), the use of different cobalt-based electrolytes does not alter the light harvesting properties of the device as the shape of the spectra is the same and the absorption onset started at 700 nm. Moreover, the electron transport layers for both devices are mesoporous TiO_2 films which means that the electron injection and collection for both devices should be the same. Therefore, MY14 possesses the same regeneration efficiency as the $\text{Co(bpy)}_3(\text{PF}_6)_2$ -based electrolyte.

The significant difference in photovoltaic parameters for both devices is the V_{oc} . The device using $\text{Co(bpy)}_3(\text{PF}_6)_2$ -based electrolyte displays 900 mV whereas the device with MY14 electrolyte exhibits only 764 mV. V_{oc} in DSCs is defined as the difference in

energy level between the Fermi level of the conduction band in TiO_2 and the redox potential of electrolyte. As determined from the CV, the redox potentials of $\text{Co(bpy)}_3(\text{PF}_6)_2$ and MY14 are 0.56 and 0.41 V vs NHE, respectively. Therefore, the difference in V_{oc} corresponded to the difference of redox potential between these two electrolytes which is 150 mV.

Figure 52. (a) Photocurrent-voltage characteristics and dark currents of C218-sensitized devices with $\text{Co(bpy)}_3(\text{PF}_6)_2$ or MY14 as electrolyte. (light intensity: $100\text{mW}\cdot\text{cm}^{-2}$, AM1.5G). (b) IPCE spectra of C218-sensitized devices with $\text{Co(bpy)}_3(\text{PF}_6)_2$ or MY14 as electrolyte.

7.3 Impedance and photocurrent transient study

The purpose of introducing the isopropyl group onto the 2-(1*H*-imidazol-2-yl)pyridine ligand has to reduce the recapture of electrons by cobalt redox mediators. To investigate the extent of recombination, the recombination resistance of the device was measured using electrochemical impedance spectroscopy. The chemical capacitance and recombination resistance of the devices with $\text{Co(bpy)}_3(\text{PF}_6)_2$ and MY14 as electrolytes measured under illumination are depicted in Figure 53.

Figure 53. (a) Chemical capacitance and (b) recombination resistance of C218-sensitized solar cells with Co(bpy)PF₆ and MY14 as electrolytes.

The chemical capacitances of TiO₂ in the two devices were compared and it can be seen that the chemical capacitance was shifted to a lower potential when MY14 was used as the electrolyte in the device. The chemical capacitance is measured with respect to the redox potential of the hole transporter [31]. The shift in the chemical capacitance was, therefore, caused by the relatively negative redox potential of the electrolyte. The difference in redox potential of these two redox couples is 150 mV, which is in agreement with the shift in the chemical capacitance of TiO₂ in the two devices. The chemical capacitance of TiO₂ in the device using MY14 is shifted until it overlaps the chemical capacitance of TiO₂ in the control device in order to eliminate the effect of conduction band position. In the recombination resistance plot, it is revealed that the recombination resistance of the device with MY14 as electrolyte is higher than the control device. This is probably due to the presence of the steric bulky isopropyl group in MY14, which could further prevent the electron recapture by the oxidized species of redox mediators. Although the overall efficiency of the device with MY14 as electrolyte does not outperform the control sample, mainly due to the redox potential level that limits the V_{oc} of the device, the recombination resistance using MY14 becomes higher than using the conventional Co(bpy)PF₆-based electrolyte.

A photocurrent transient measurement was carried out to investigate the mass transport of the electrolyte in the device. The transient photocurrent spectrum of the C218-sensitized DSCs with two different electrolyte systems is given in Figure 54. When the device is illuminated, there is a rise in photocurrent, subsequently followed by J_{sc} decay before reaching the saturated photocurrent density. Once the device is illuminated, the well distributed Co^{3+} species around the sensitizers regenerate the photo-oxidized sensitizers immediately after the electron is injected into the conduction band of TiO_2 without mass transport limitations and produces the maximum photocurrent. Under constant illumination, slower mass transport of Co^{3+} species causes insufficient dye regeneration, which consequently reduces the photocurrent density. This is a common issue for cobalt-based redox couples as the molecular size is comparatively larger than the I^-/I_3^- redox mediators. Both devices exhibit similar photocurrent response upon illumination, indicating the introduction of isopropyl group in MY14 does not hinder the transport of redox couples for dye regeneration.

Figure 54. Photocurrent transient of C218-sensitized DSCs with Co(bpy)PF_6 and MY14 as electrolytes.

7.4 Summary

In this chapter, the design and synthesis of a new cobalt-based redox couple, MY14, has been demonstrated. Its application as the redox couple in DSCs has also been shown. MY14 is formed by a single step alkylation with high yield. The low optical absorption of MY14 allows it to be a potential redox couple which does not compete with photosensitizers in light harvesting. The use of MY14 electrolyte does not change the light absorption profile as determined from its IPCE.

The introduction of the bulky isopropyl group in the structure of ligand enables better prevention of interfacial recombination, which has been observed from the higher recombination resistance measured by impedance spectroscopy. The redox potential of the redox couple is tuned by introducing the isopropyl group, which is considered as a weak donating group. This provides an alternative choice for other sensitizers with higher HOMO level (more negative potential) which could minimize the potential loss in the device. Surprisingly, the presence of bulky steric hindrance in the ligand does not cause any mass transport limitation, as compared to the control device using Co(bpy)PF₆ as electrolyte. This is important as severe mass transport limitation could reduce the J_{sc} and cause detrimental effect to the overall efficiency. In C218-sensitized DSCs, it was realized that a comparable J_{sc} is obtained from MY14 electrolyte, however, lower V_{oc} is observed which is mainly due to the difference in redox potentials of these two electrolytes. Overall, this is an interesting redox couple which possesses lower recombination with electrons in the conduction band of TiO₂.

It has been known that the main drawback in liquid DSCs is the use of volatile solvent in preparing the electrolyte. The feasible solution is to replace the volatile electrolyte by spiro-OMeTAD, a solid state hole conductor with deeper redox potential than iodide/triiodide and cobalt-based electrolyte which could generate higher photovoltage. In the following chapter, the use of new cobalt-based dopant for spiro-

OMeTAD for enhancing its conductivity as well as generating high photovoltage will be demonstrated.

Chapter 8

Enhanced charge transfer of spiro-OMeTAD in perovskite solar cells

One of the main drawbacks of commercializing liquid based DSCs is its corrosive and volatile I/I_3^- electrolyte, which could potentially corrode the metal contact or leak out from the devices. A feasible solution is to replace the liquid electrolyte with a solid state hole conductor which performs the same function in DSCs, *i.e.* conducting holes to the counter electrode. Several conductive polymers and hole transporting materials have been used in DSCs to address the stability issue, such as PEDOT, P3HT, PANI and CuSCN [132-135]. Among all these hole conductors, the most successful and widely used hole transporting material in solid-state DSCs is 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)9,9'-spirobifluorene (spiro-OMeTAD) [80] and its chemical structure is depicted in Figure 55(a). The redox potential of spiro-OMeTAD is 0.72 V *vs* NHE which is more positive compared to I/I_3^- (0.35 V *vs* NHE) and $\text{Co}^{2+/3+}(\text{bpy})_3$ (0.56V *vs* NHE). This further reduces the loss in the potential loss for regeneration. However, the pristine form of spiro-OMeTAD exhibits low conductivity which significantly influences the photocurrent density and fill factor of the devices and leads to lower power conversion efficiency [136, 137]. To improve the conductivity of spiro-OMeTAD, more charge carriers should be induced by doping the hole transporter which is crucial for improving the photovoltaic performance of solid-state DSCs (ssDSCs).

Figure 55. Chemical structures of spiro-OMeTAD, FK102 and MY11 dopants.

In earlier work, chemical doping of spiro-OMeTAD was done by using $\text{N}(\text{PhBr})_3\text{SbCl}_6$ as the chemical dopant and an overall power conversion efficiency of 0.74% was attained [80]. It has also been shown that oxidized spiro-OMeTAD can be generated in the presence of molecular oxygen and lithium salts under illumination [81]. However, the doping of spiro-OMeTAD using molecular oxygen is challenging as the control of the doping level is difficult and hence reproducibility is hard to achieve. Therefore, chemical doping of spiro-OMeTAD is needed.

High efficiency solid-state DSCs (7.2%) have been demonstrated in Y123-sensitized devices, whereby tris(2-(1H-pyrazol-1-yl)pyridine)cobalt(II) bis(hexafluorophosphate) (FK102) was used as a p-dopant for spiro-OMeTAD [82]. The driving force for the one-electron oxidation reaction of spiro-OMeTAD is the energy difference between the HOMO of spiro-OMeTAD and the redox potential of FK102. The difference in the energy level allows the electron to transfer from spiro-OMeTAD to FK102, whereby the oxidized species of spiro-OMeTAD (spiro-OMeTAD^+) is created. Hence, the conductivity of the hole conducting layer is improved by the increasing amount of spiro-OMeTAD^+ .

The advantage of using chemical doping is the potential reproducibility of the fabricated devices. However, the photovoltaic performance could be affected by the presence of unreacted chemical dopants due to non-ideal doping efficiency. On the other

hand, the reacted dopants will still remain in the hole transporting layer after the doping reaction as “defects”, which could have potentially detrimental effects on the device. Therefore, it is important to reduce the amount of dopant used, thus reducing the “defects” in the device. One of the ways to reduce the amount of dopant, while maintaining the high efficiency of the devices, is to enlarge the driving force for the charge transfer reaction between spiro-OMeTAD and dopants to ensure high spiro-to-spiro⁺ conversion.

Lately, much effort has been put into the research on developing high efficiency solar cells based on organic-inorganic halide (CH₃NH₃PbI₃) perovskite materials [84, 138, 139]. Due to its sufficiently low energy band gap [85] and remarkably long exciton diffusion length [88, 89], high efficiency perovskite based solar cells have been achieved using different strategies for depositing the materials, doping the electron collector, and using various types of hole conductors [86, 93, 94, 96, 140]. Using a hole conductor with deep HOMO level is one of the methods to minimize the voltage loss and so enhance the V_{oc} of the device. To ensure a better performance of the hole transporting material, the development of dopants with a deeper redox potential becomes essential.

In this chapter, a high V_{oc} in a solid state perovskite solar cell was obtained by using spiro-OMeTAD, doped by the new cobalt-based p-type dopant, tris[2-(1*H*-pyrazol-1-yl)pyrimidine]cobalt(III) tris[bis(trifluoromethylsulfonyl)imide] (MY11). The synthesis and electrochemical property are discussed.

8.1 Design and synthesis of dopant

In the previous chapter, it has been described how the incorporation of an electron donating group will negatively shift the redox potential of a cobalt complex. In the case of cobalt-based dopants, the charge transfer reaction occurs, depending on the driving force which refers to the difference in energy level between HOMO of spiro-OMeTAD and redox potential of dopant. Hence, to obtain a more positive redox potential as

compared to the HOMO of spiro-OMeTAD, a strong electron withdrawing ligand is preferred.

In the synthesis of a cobalt-based electrolyte with a lower redox potential, it has been shown that replacing the pyridine moiety with a pyrazole moiety in the ligand enables a positive shift in the redox potential of the metal complex, as pyrazole is a stronger π -acceptor when compared to pyridine [43]. By incorporating the pyrazole moiety in the structure of ligands, various cobalt complexes have been synthesized and utilized as redox mediators [40] and dopants [82, 83, 141] in DSCs. It has to be highlighted that among these dopants, 7.2% power conversion efficiency has been achieved in solid-state DSCs which used FK102 as dopant along with highly absorbing organic dyes [82]. Therefore, in order to ensure a deep redox potential in cobalt complex, the pyrazole moiety is kept in the ligand structure while another electron withdrawing unit is introduced, which is expected to further tune the redox potential to a more positive region. In Figure 56, the synthetic procedures of the particular ligand and dopant (MY11) are illustrated. The coupling reaction between 2-chloropyrimidine and pyrazole is carried out under basic condition. Pyrazole is deprotonated by using potassium *tert*-butoxide, which is subsequently coupled with a pyrimidine unit *via* S_N2 reaction. The desired ligand, 2-(1*H*-pyrazol-1-yl)pyrimidine, was obtained in a yellowish oily form.

Figure 56. Synthetic routes of ligand and MY11 dopant.

The MY11 dopant is synthesized from reacting stoichiometric amounts of ligand and cobalt(II) chloride (3:1) in methanol. It is worth mentioning that the cobalt precursor was added slowly into the methanolic solution containing ligands to avoid any formation of polymeric structures. To obtain the solid, precipitation was achieved by using lithium bis(trifluoromethane)sulfonimide (LiTFSI). This salt was used rather than NH_4PF_6 for improving the solubility of the complex which allows it to interact better with spiro-OMeTAD in solution and more importantly, this compound has higher electrochemical stability [142]. The corresponding cobalt complex was formed and obtained as orange solid. The powder is further oxidized using a strong oxidant, nitrosyl tetrafluoroborate (NOBF_4), which converts the cobalt(II) into cobalt(III) complex. MY11 was finally obtained as an orange solid and the chemical structures of MY11 and conventional dopant for spiro-OMeTAD, FK102, are depicted in Figure 55. The device performances of devices using MY11 were compared to the one using FK102 (control devices).

8.2 Charge transfer reaction between dopant and spiro-OMeTAD

The redox potential of MY11 was examined through cyclic voltammetry. The cyclic voltammograms of spiro-OMeTAD, FK102 and MY11 are shown in Figure 57(a). It can be clearly observed that the redox potential of MY11 is shifted to a more positive potential as compared to FK102. The HOMO level of spiro-OMeTAD is 5.12 eV and the redox potential of FK102 and MY11 are 5.48 eV and 5.77 eV, respectively. The schematic energy diagram of $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based solar cell is illustrated in Figure 57(b).

As compared to FK102, the pyridine moiety was replaced by a pyrimidine core in MY11 in order to tune the redox potential more positively. It has been shown that electron withdrawing groups, such as chloride and nitro substituents could be introduced to modulate the redox potential of metal complexes.[47] In the case of MY11, there is an

uncoordinated nitrogen atom located in the pyrimidine moiety in the ligand, which provides electron withdrawing effect to the cobalt complex, offering a 290 mV shift in potential away from FK102. It could be estimated that each ligand provides an approximately 100 mV shift in potential.

Figure 57. (a) Cyclic voltammogram of spiro-OMeTAD, FK102 and MY11. (b) Schematic energy diagram of CH₃NH₃PbI₃ based solar cells using spiro-OMeTAD as hole conductor. The red arrow indicates the driving forces for doping of spiro-OMeTAD using MY11.

In the conventional combination of spiro-OMeTAD and FK102, there is a driving force of 360 mV for one-electron oxidation reaction which is in agreement with the reported value [82, 83]. For the combination of spiro-OMeTAD and MY11, the driving force increases significantly to 650 mV. The higher driving force for the doping reaction could lead to a higher concentration of spiro-OMeTAD⁺ as the same amount of dopants (FK102 and MY11) are used.

The one-electron charge transfer reaction between spiro-OMeTAD and cobalt dopants could be monitored *via* optical absorption spectroscopy. The optical absorption spectra of spiro-OMeTAD with electrolyte additives and different dopants are displayed in Figure 58(a). Upon adding LiTFSI, no absorption band for spiro-OMeTAD⁺ was observed, which is similar to an earlier report [143]. Generally, the absorption band of spiro-OMeTAD⁺ was found at approximately 520 nm [144]. Upon adding the cobalt dopant, an absorption band around 520 nm was observed, which is attributed to the absorption of spiro-OMeTAD⁺. Comparing the absorption spectra of spiro-OMeTAD with FK102 and MY11, it can be realized that the absorption band of spiro-OMeTAD⁺, which is between 400 to 600 nm, is more intense in MY11, although the same amount of dopants are used. This implies that a higher spiro-to-spiro⁺ conversion efficiency is found for MY11 as it possesses a higher driving force for the charge transfer reaction than FK102. In Figure 58(b), it can be seen that the absorption of spiro-OMeTAD⁺ is increased while the absorption band at ~390 nm is decreased upon gradual addition of MY11.

As previously mentioned, the pristine spiro-OMeTAD exhibits low conductivity, which results in the increase in the total series resistance of the device, and restricts the performance of the solid-state solar cells. The effect of chemical doping on the conductivity of spiro-OMeTAD can be examined *via* 4 probe conductivity measurements. The conductivity of pristine spiro-OMeTAD was compared to the doped spiro-OMeTAD using FK102 and MY11. The results of the conductivity measurements are shown in Table 8. The pristine spiro-OMeTAD displays a low conductivity of $5.21 \times 10^{-6} \text{ S cm}^{-1}$ which is in agreement with the reported values [82, 143]. In order to understand the conductivity of the hole transporting layer in the device, 15.8 mol% of dopant is added to the spiro-OMeTAD solution which is the same doping concentration as in the device fabrication. The conductivity of the doped spiro-OMeTAD film is drastically improved

to 1.35×10^{-4} and $1.69 \times 10^{-4} \text{ S cm}^{-1}$ by using FK102 and MY11, respectively. As a result, the conductivity of spiro-OMeTAD film could be improved by two orders of magnitude higher than the pristine form of spiro-OMeTAD upon doping with MY11.

Figure 58. (a) UV-vis absorption spectra of spiro-OMeTAD with additives (LiTFSI and TBP) and dopants (FK102 or MY11). Inset shows the enlarged spectra of the oxidized spiro-OMeTAD peak at around 524 nm. (b) Optical absorption of spiro-OMeTAD solution with a gradual increase of dopant concentration.

It is worth mentioning that the conductivity of the MY11-doped spiro-OMeTAD film is slightly higher as compared to that of FK102-doped spiro-OMeTAD. This can be rationalized by the larger driving force for charge transfer reaction which could lead to higher spiro-to-spiro⁺ conversion as ascertained in this section. The results of conductivity measurements are in agreement with the optical absorption measurements, which show a greater amount of spiro-OMeTAD⁺ species is created by using MY11 as

chemical dopant. Due to its higher spiro-to-spiro⁺ conversion capability, it allows the reduction in the amount of MY11 used for fabrication, which could reduce the unwanted “defects” in the device.

Table 8. Comparison of conductivity of undoped and doped spiro-OMeTAD films (with 15.8 mol% FK102 or MY11) on glass substrates.

	Conductivity (S cm^{-1})
Pristine spiro	5.21×10^{-6}
Spiro + FK102	1.35×10^{-4}
Spiro + MY11	1.69×10^{-4}

8.3 Photovoltaic characteristics

The function of MY11 on device performances for spiro-OMeTAD was investigated in solid state perovskite solar cells. The device configuration is depicted in Figure 59. Briefly, a compact TiO_2 blocking layer was deposited by spray pyrolysis and a mesoporous nanocrystalline TiO_2 layer was spun-coated on top of the blocking layer. The perovskite absorber was formed on the mesoporous TiO_2 layer from sequential deposition technique, whereas the hole conductor, spiro-OMeTAD, is deposited on the absorber layer. Lastly, a thin gold contact is deposited by thermal evaporation. The photovoltaic performances of the solar devices using undoped and FK102- or MY11-doped spiro-OMeTAD are summarized in Table 9 and the corresponding I - V curves are displayed in Figure 60.

Figure 59. Device configuration of solid state organic inorganic perovskite solar cell: FTO/compact TiO_2 layer/mesoporous TiO_2 layer: $\text{CH}_3\text{NH}_3\text{PbI}_3$ /spiro-OMeTAD/Au.

Table 9. *I-V* characteristics of $\text{CH}_3\text{NH}_3\text{PbI}_3$ devices using different dopants for spiro-OMeTAD. A total of 12 devices were fabricated and tested.

	15.8 mol% FK102	15.8 mol% MY11	8.0 mol% MY11	Undoped
J_{sc} [mAcm^{-2}]	16.80 ± 0.21	16.80 ± 0.19	17.20 ± 0.20	7.35 ± 0.45
V_{oc} [mV]	965 ± 12	1000 ± 10	927 ± 12	867 ± 18
FF	0.68 ± 0.01	0.71 ± 0.01	0.71 ± 0.01	0.56 ± 0.04
η (%)	11.0 ± 0.16	11.9 ± 0.15	11.3 ± 0.17	3.56 ± 0.11

Figure 60. Photocurrent-voltage characteristics and dark currents of $\text{CH}_3\text{NH}_3\text{PbI}_3$ representative devices using spiro-OMeTAD with different dopants (light intensity: 100mWcm^{-2} , AM1.5G).

The device undoped spiro-OMeTAD is considered as the control device and compared to the devices using doped spiro-OMeTAD. The control device displays only 3.56% with low photocurrent, probably due to its low conductivity in its pristine form. With FK102-doped spiro-OMeTAD, a power conversion efficiency of 11% with J_{sc} of $16.8\text{ mA}\cdot\text{cm}^{-2}$, V_{oc} of 965 mV and FF of 0.68 was achieved. In the device with MY11, the device efficiency is further improved to 11.9% which is mainly due to the improvement in all photovoltaic parameters. In solid-state DSCs, the V_{oc} of a device is produced by the energy difference between the Fermi level of TiO_2 and the HOMO level of spiro-OMeTAD [80]. In comparison, the V_{oc} is enhanced from 965 mV in the device with FK102 to 1000 mV in the device with MY11. This is probably due to the increased concentration of spiro-OMeTAD^+ in the hole transporting layer which has been ascertained by measuring the optical absorption of doped spiro-OMeTAD. The increased

hole concentration may induce a potential shift of Fermi energy level towards the HOMO level of spiro-OMeTAD. This shift enlarges the difference between the two energy levels, which results in higher V_{oc} [145]. On the other hand, the improved fill factor in MY11 containing devices could originate from the additional charge carriers, which are created by doping reaction, leading to higher conductivity and reducing the total series resistance of the device. In these devices, comparable J_{sc} are obtained, indicating no significant difference in collection and injection efficiency. In Figure 61(a), the molar absorptivities of FK102 and MY11 are low, which does not affect the light harvesting ability of the perovskite absorber and high photocurrent is obtained. From the IPCE spectra, illustrated in Figure 61(b), no significant loss can be observed when FK102 is replaced by MY11 as the dopant.

Figure 61. (a) UV-vis absorption spectra of FK102 and MY11 in acetonitrile. (b) IPCE of perovskite-based devices with different dopant concentrations.

As there is a larger driving force for doping the spiro-OMeTAD molecules, it allows the reduction of M11 doping concentration in the devices. From Table 9, when the doping concentration is reduced to 8 mol%, the V_{oc} of the device decreased to 927 mV. This could be due to the concentration of spiro-OMeTAD⁺ being lesser as compared to the device with 15.8 mol% of MY11, which causes the loss in potential. Interestingly, the fill factor of the device is still maintained as high as in 15.8 mol% of MY11 although

the doping concentration is reduced. Surprisingly, the overall conversion efficiency of the device with 8 mol% of MY11 still outperforms the device with 15 mol% of FK102, which is mainly due to the improvement in fill factor.

8.4 Summary

In this chapter, a high photovoltage in devices was obtained by using MY11-doped spiro-OMeTAD. Compared to FK102, MY11 exhibits a higher driving force for the charge transfer reaction due to its more positive redox potential. MY11 was designed by introducing a pyrimidine moiety to the structure of the ligand. The uncoordinated nitrogen atoms in this moiety serve as electron withdrawing components, which tune the redox potential of MY11 to be 290 mV more positive than FK102. In addition, the conductivity of the MY11-doped spiro-OMeTAD was increased two orders of magnitude as compared to the pristine form of spiro-OMeTAD.

The effect of using MY11 as p-dopant is demonstrated in perovskite solar cell and 12% power conversion efficiency is demonstrated. The main improvement comes from the V_{oc} and fill factor. Higher spiro-to-spiro⁺ conversion was found in MY11 and results in higher V_{oc} where the Fermi level is shifted towards the HOMO level of spiro-OMeTAD by the increased concentration of spiro-OMeTAD⁺. High spiro-to-spiro⁺ conversion would also allow the reduction of MY11 used in the device to avoid the undesirable “defects” after the doping reaction. Surprisingly, by reducing the doping concentration to 8 mol%, the efficiency of the MY11-doped devices still outperformed the FK102-doped devices with 15.8 mol% doping concentration.

Among all the current cobalt-based dopants for spiro-OMeTAD to date, MY11 still possesses the deepest (positive in potential) redox potential, which allows it to be a potential candidate as p-dopant for a wide range of hole transporting materials in photovoltaic applications.

Chapter 9

Conclusions and future recommendations

9.1 Conclusions of thesis

Modulating interfacial recombination and mass transport limitation through electrolyte additive

The key challenge of utilizing Co(II/III) redox electrolytes in DSCs is the prevention of interfacial recombination between electrons in charge transport layer and electrolyte. The possible solution to enhance the interfacial recombination is modulating the electrolyte additive which directly contacts with the surface of the semiconductor. It has been determined that the presence of TBP as an electrolyte additive in cobalt-based electrolyte improved the V_{oc} of the device by (1) upshifting the conduction band of TiO_2 and (2) enhancing recombination resistance. Through electrochemical impedance spectroscopy, it was concluded that the shift in the conduction band of TiO_2 contributes approximately 67% of the V_{oc} improvement. The optimal concentration of TBP for cobalt-based electrolyte is 0.4 M. However, the photocurrent density of the device is gradually decreased by approximately 14%, as the TBP concentration is increased. The possibility of having difficulty in electron injection has been eliminated by using a sensitizer possessing high HOMO energy level. By deriving the viscosity from the Einstein-Stokes equation, it was found that the viscous nature of TBP may lead to the mass transport limitation in cobalt-based electrolytes.

Cyanobiphenyl based organic molecules have been demonstrated as promising electrolyte additives for cobalt-based electrolytes. Addition of this additive benefits the V_{oc} from negatively shift of the conduction band of TiO_2 as well as reduction of TiO_2 /electrolyte interfacial recombination. The cyanobiphenyl compounds with longer

molecular structures compared to TBP perform better than TBP in preventing the electron recapture by oxidized species of redox couples. Interestingly, addition of these cyanobiphenyl compounds does not lead to any diffusion limitation, while reducing the interfacial recombination, and guarantee higher V_{oc} . Moreover, incorporation of these compounds in electrolyte does not increase the charge transfer resistance and disturb the chemical stability of the devices. The best performing device exhibits a power conversion efficiency of 6.22%. Incorporating the cyanobiphenyl compounds in electrolyte shows a 13.2% improvement in V_{oc} as compared to the device using the electrolyte containing only TBP. The exciting finding of utilizing cyanobiphenyl compounds as an electrolyte additive offers a way to achieve high efficiency solar cells using cobalt-based redox mediators.

Controlling electron recapture by surface passivation and structural modification of cobalt(II/III) redox shuttles

The TiO_2 surface and the oxidized species of redox couples are the main sites for recombination in DSCs. It is important to modify the surface of TiO_2 and the chemical structure of redox shuttles in retarding the electron recapture. Alkanephosphonic acid has been demonstrated as a potential surface adsorber to passivate the TiO_2 surface which helps to restrict the recombination. The alkanephosphonic acid treated TiO_2 electrode improved all photovoltaic parameters of the device. The improvement in photocurrent density is attributed to the better charge collection efficiency in phosphonic acid grafted devices. The V_{oc} of the device is also improved as well as its fill factor. Results derived from EIS have shown that the recombination resistance of the device is significantly enhanced due to the blocking effect from the alkanephosphonic acid on the TiO_2 surface. Although structural modification may incorporate long alkyl chains into the molecular

structures of sensitizer, it is still insufficient for the prevention of interfacial recombination existing within the cobalt(II/III) redox mediated DSCs.

Interfacial recombination could also be reduced from incorporating steric bulky hindrance into the structure of cobalt(II/III) redox couples. One step alkylation in preparing new cobalt redox shuttles, MY14, and its low optical absorption allows it to be a potential electrolyte for DSCs. The introduction of the bulky isopropyl group to the structure of the ligand prevents the cobalt(III) species from easily recombining with the electron in the conduction band of TiO₂. Higher recombination in devices using MY14 electrolyte highlighted the importance of structural modification in reducing interfacial recombination. Surprisingly, the presence of bulky hindrance in the ligand does not cause any mass transport limitation, as compared to the control device using Co^{2+/3+}(bpy)₃ as electrolyte. The more negative redox potential in MY11 does not produce a higher Voc compared to Co^{2+/3+}(bpy)₃, however, this provides an alternative choice for other sensitizers with higher HOMO level to minimize the loss in overpotential.

Directing charge transfer in spiro-OMeTAD by chemical doping using new cobalt(III) complex with deep redox potential

Replacing liquid electrolyte with solid state hole conductor, spiro-OMeTAD, leads to the development of solid state DSCs. This hole conductor possesses a more positive redox potential than iodide/triiodide and cobalt(II/III) redox system, which is beneficial for reducing the loss in overpotential. However, the pristine form of spiro-OMeTAD displays poor conductivity, which is detrimental for charge transport. Chemical doping is performed using a new cobalt(III) complex, MY11, and the conductivity is increased two orders of magnitude. Due to the larger driving force for the one-electron oxidation reaction, a higher amount of spiro-OMeTAD⁺ is generated, which leads to the Fermi level shifted towards the HOMO level of the spiro-OMeTAD and

consequently yields higher V_{oc} . The high spiro-to-spiro⁺ conversion allows a reduction of dopant to be used to avoid undesirable “defects” in the device. Interestingly, the device with 8% MY11 dopant performs better than those with 15.8% FK102 dopant. It is worth highlighting that MY11 exhibits the deepest redox potential among the current cobalt-based dopant, making it a promising p-dopant for a wide range of HTM in photovoltaic applications.

9.2 Future outlook

Tuning of redox potential by ligand modification

Other than by engineering the surface properties to reduce interfacial recombination, V_{oc} can also be enhanced by tuning the redox potential of cobalt complexes *via* structural modification. As has been discussed in chapter 7, imidazole-based ligands are a suitable ligand due to their ease of structural modification through the substitution of the amine.

Although the 2-(1*H*-imidazol-2-yl)pyridine ligand successfully enhances the recombination resistance, a lower V_{oc} is still observed in the device mainly due to the redox potential level being higher than that of the $Co^{2+/3+}(bpy)_6$ redox couple. To lower the redox potential of the cobalt complex, the 2-(2-pyridyl)benzimidazole ligand is one option in that it possesses a similar chemical structure to 2-(1*H*-imidazol-2-yl)pyridine ligand with the difference being the additional phenyl ring is fused to the imidazole moiety. This additional phenyl ring serves as an electron withdrawing group and the redox potential of the desired cobalt complex is positively tuned. This effect was rationalized by comparing $Co^{2+/3+}(bpy)_3$ and $Co^{2+/3+}(phen)_3$ where their redox potentials are 0.52 V and 0.62 V *vs* NHE, respectively (see Figure 62 for the chemical structures).

Figure 62. Chemical structures of (a) 2-(1H-imidazol-2-yl)pyridine, (b) 2-(2-pyridyl)benzimidazole, (c) 2,2'-bipyridyl (bpy) and (d) 1,10-phenanthroline (phen).

As a continuation of the work from chapter 7, alkylation on 2-(2-pyridyl)benzimidazole would yield ligand **L1**, see Figure 63. It would be quite interesting to observe the redox couples obtained using this ligand. The recombination resistance should be remarkably enhanced by the bulky isopropyl groups. On the other hand, the mass transport property should also be investigated as the additional phenyl in the ligand could also lower the diffusivity. A fluorinated isopropyl group is another potential substituent for modifying the ligand. Ligands **L2** and **L3** are thus proposed due to their unique structural properties. It is well-known that fluorine is the most electronegative element. Coupling heptafluoro-2-iodopropane onto the ligand could further induce the shift of redox potential in a positive direction due to the electron withdrawing ability of the fluorines. When the cobalt complex is formed, the fluorine atoms would provide partial negative charges on the outer sphere and this could lead to reduced interfacial recombination due to electron repulsive forces. All of these ligands are designed for achieving high photovoltage in solar cells.

Figure 63. Proposed ligands for new cobalt(II/III) redox couples.

Multiple-electron oxidation reaction of spiro-OMeTAD

The chemical doping is important to enhance the electronic properties of hole conductors, especially in promoting their conductivity. The current cobalt-based dopant could only have one-electron charge transfer reaction where the spiro-OMeTAD is oxidized into spiro-OMeTAD⁺ while Co(III) complex is reduced to Co(II).

It could be more efficient if the dopant could accept more than one electron from spiro-OMeTAD during the charge transfer reaction. Nickel has common oxidation states of +2 and +4. The nickel(IV) complexes are potentially useful as chemical dopants for spiro-OMeTAD. If one nickel complex can undergo two one-electron charge transfer reaction with two spiro-OMeTAD molecules, the amount of dopant used for the doping reaction could be reduced 50%. The significantly reduced amount of dopant used will increase the purity of the HTM layer, which facilitates the charge transport within the device.

The key factor in charge transfer is the appropriate energy level alignment between dopant and HTM. One of the methods to bring down the redox potential of dopant is coordinating strong electron withdrawing ligands to the metal center. In this thesis, it has been demonstrated that pyrazole moiety is a good π -acceptor as well as pyrimidine moiety. For future study, a stronger electron withdrawing ligand, 2-(1*H*-pyrazol-1-yl)pyrazine, could be used to prepare a new dopant with a deeper redox potential. A proposed complex is given in Figure 64.

Figure 64. A proposed chemical structure of a metal complex for the synthesis of a dopant with a deeper redox potential.

Patent

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Publications

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2. **Koh Teck Ming**, Li Hairong, Kazuteru Nonomura, Nripan Mathews, Anders Hagfeldt, Michael Grätzel, Subodh G. Mhaisalkar and Andrew C. Grimsdale, Photovoltage enhancement from cyanobiphenyl liquid crystals and 4-*tert*-butylpyridine in Co (II/III) mediated dye-sensitized solar cells, Chemical Communications, 49, 9101-9103, 2013.
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