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Sarah Holliday

Synthesis and Characterisation of Non-Fullerene Electron Acceptors for Organic Photovoltaics

Doctoral Thesis accepted by
the Imperial College London, UK

 Springer

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Supervisor's Foreword

Sarah Holliday's thesis addresses the fundamentals of designing high-efficiency electron-accepting molecules for organic solar cells. It would not be an overstatement to contest that the two main manuscripts that have arisen from the Ph.D. (Holliday et al., "High-efficiency and air-stable P3HT-based polymer solar cells with a new non-fullerene acceptor," *Nat. Commun.* 2016, 7, 11585; Holliday et al., "A rhodanine flanked non-fullerene acceptor for solution-processed organic photovoltaics," *J. Am. Chem. Soc.* 2015, 137, 898–904), cited already over 190 and over 180 times, respectively, have enabled the field to replace fullerenes as the dominant electron acceptors in organic photovoltaics. Her design guidelines have been instrumental in the resurgence of organic solar cell research, inspired by the high performance of her materials.

The thesis specifically reports the design, synthesis and characterization of small molecule electron acceptors for polymer solar cells. The prospect of realising cheaper and more energy efficient solar cells using organic semiconductors has motivated intense research in this area over the past decade. In this thesis, an innovative small molecule acceptor design was introduced that can be used to replace the fullerene acceptors currently employed in most polymer solar cells. It was demonstrated that the structural, electrochemical and optical properties of this material can be effectively tuned via small changes to the molecular structure. A new family of acceptor materials was subsequently presented which have improved photovoltaic performance compared to fullerene acceptors in solar cell devices with a range of polymer donor materials, most notably with the ubiquitous poly(3-hexylthiophene) (P3HT). Detailed optoelectronic and morphological studies of the donor-acceptor blends were used to offer important insights into the origin of this improved photovoltaic performance, leading to the proposal of fundamental design principles for non-fullerene small molecule acceptors that have been widely used to promote further advancements in this field. In addition, these new materials demonstrate improved air stability compared to many other high performing polymer solar cells, offering real potential for commercially scalable technology.

London, UK
February 2018

Prof. Iain McCulloch

Abstract

Recent years have witnessed remarkable advances in the field of organic photovoltaics (OPV). Efficiencies over 10% have now been demonstrated, partly due to the development of new, low bandgap donor polymers. The majority of these OPV devices employ a fullerene derivative as the electron-accepting component in the active layer. While fullerenes are excellent acceptors in terms of electron mobility, electron affinity and ability to form suitable bulk heterojunction morphologies, they also have some limitations. These include limited absorption in the visible and near-IR region of the electromagnetic spectrum, poor tunability in terms of energy levels and absorption, and morphological instability. For these reasons, many researchers are seeking to develop alternative acceptors for OPV.

This thesis focuses on the design, synthesis and characterisation of small molecule, non-fullerene acceptors. Initially, C_3 -symmetric truxenone derivatives were developed, which demonstrated broad absorption and the ability to carefully tune the frontier energy levels of the molecule. However, it appeared that the poor electron mobility, as well as an unfavourable morphology due to large-scale crystallisation of the acceptor, limited device performance. The second part of this thesis explores linear small molecules with rhodanine end groups, which also demonstrated an excellent ability to tune the frontier energy levels through changes to the chemical structure. Compared with the truxenones, these acceptors were relatively amorphous and formed a more favourable, intermixed morphology with the polymer poly(3-hexylthiophene) (P3HT). Device efficiencies of 4.1% were achieved with this blend; however, performance was again limited by microstructure, which in this case was slightly too intermixed, leading to recombination losses. In addition, the lack of complementary absorption of the donor and acceptor reduced the amount of photocurrent that could be generated. The third section of this thesis describes how the molecular structure of this acceptor was modified to overcome both of these issues, by the replacement of a 9,9'-dioctylfluorene core unit with indacenodithiophene, leading to a more planar molecular structure. The increased crystallinity and red-shifted absorption of this acceptor resulted in an

improved efficiency of 6.4%, which at the time of writing is the highest efficiency for non-fullerene devices with P3HT. In addition to high efficiency, these devices also had improved air stability compared to P3HT:fullerene devices as well as devices with high-performance donor polymers, demonstrating the real potential application for these materials in commercialisable OPV technology.

Parts of this thesis have been published in the following journal articles:

S. Holliday, R. S. Ashraf, A. Wadsworth, D. Baran, S. A. Yousaf, C. B. Nielsen, C.-H. Tan, S. D. Dimitrov, Z. Shang, N. Gasparini, M. Alamoudi, F. Laquai, C. J. Brabec, A. Salleo, J. R. Durrant and I. McCulloch, **“High-efficiency and air-stable P3HT-based polymer solar cells with a new small molecule acceptor”** *Nat. Commun.*, 2016, **7**, 11585.

C. B. Nielsen, S. Holliday, H.-Y. Chen, S. Cryer and I. McCulloch, **“Non-fullerene small molecule electron acceptors for organic solar cells”** *Acc. Chem. Res.*, 2015, **48**, 2803.

S. Holliday, R. S. Ashraf, C. B. Nielsen, M. Kirkus, J. A. Röhr, C.-H. Tang, E. Collado-Fregoso, A.-C. Knall, J. R. Durrant, J. Nelson and I. McCulloch, **“A rhodanine flanked nonfullerene acceptor for solution-processed organic photovoltaics”** *J. Amer. Chem. Soc.*, 2015, **137**, 898.

C. B. Nielsen, E. Voroshazi, S. Holliday, K. Cnops, D. Cheyns and I. McCulloch, **“Electron deficient truxenone derivatives and their use in organic photovoltaics”** *J. Mater. Chem. A*, 2014, **2**, 12348.

C. B. Nielsen, E. Voroshazi, S. Holliday, K. Cnops, B. P. Rand and I. McCulloch, **“Efficient truxenone-based acceptors for organic photovoltaics”** *J. Mater. Chem. A*, 2013, **1**, 73.

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Abbreviations

AFM	Atomic force microscopy
BFI	Tetraazabenzodifluoranthene diimide
BHJ	Bulk heterojunction
BPO	Benzoyl peroxide
BT	2,1,3-benzothiadiazole
CB	Chlorobenzene
CE	Charge extraction
CELIV	Charge extraction by linearly increasing voltage
CV	Cyclic voltammetry
D-A	Donor-acceptor
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DFT	Density functional theory
DIO	1,8-diiodooctane
DME	Dimethoxyethane
DPP	Diketopyrrolopyrrole
DSC	Differential scanning calorimetry
EA	Electron affinity
E_g	Bandgap
EQE	External quantum efficiency
eV	Electron-volt
FF	Fill factor
GIXRD	Grazing incidence X-ray diffraction
HOMO	Highest occupied molecular orbital
ICBA	Indene-C ₆₀ -bisadduct
IDT	Indacenodithiophene
IP	Ionisation potential
ITO	Indium tin oxide
J_{mp}	Current at point of maximum power
J_{sc}	Short circuit current
LUMO	Lowest unoccupied molecular orbital

MO	Molecular orbital
NFA	Non-Fullerene acceptor
NMR	Nuclear magnetic resonance spectroscopy
o-DCB	Ortho-dichlorobenzene
OPV	Organic photovoltaic(s)
P3HT	Poly(3-hexylthiophene-2,5-diyl)
PC ₆₀ BM	Phenyl-C ₆₁ -butyric acid methyl ester
PC ₇₀ BM	phenyl-C ₇₁ -butyric acid methyl ester
PCE	Power conversion efficiency
PCE-10	Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b 4,5-b'] dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothiopheno[3,4-b] thiophene-)-2-carboxylate-2-6-diyl)] (a.k.a. PTB7-Th)
PCE-11	Poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3''-di (2-octyldodecyl)-2,2'5',2''5'',2'''-quaterthiophene-5,5'''-diyl)] (a.k.a. PffBT4T-2OD)
PDI	Perylene diimide
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
P _{in}	Incident light power density
PLQ(E)	Photoluminescence quenching (efficiency)
PTB7	Poly((4,8-bis[(2-ethylhexyl)oxy]benzo[1,2- <i>b</i> :4,5- <i>b'</i>] dithiophene-2,6-diyl) { 3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno [3,4- <i>b</i>]thiophenediyl))
PV	Photovoltaic
SCLC	Space charge limited current
T ₅₀	Time after which PCE falls to 50% of initial value
T ₈₀	Time after which PCE falls to 80% of initial value
TAS	Transient absorption spectroscopy
TBAPF ₆	Tetrabutylammonium hexafluorophosphate
T _c	Crystallisation temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
T _m	Melting temperature
V _{mp}	Voltage at point of maximum power
V _{oc}	Open circuit voltage
XRD	X-ray diffraction