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Synthesis, Characterization and Evaluation of Aza-dipyrromethenes and other Small Molecules for Organic Photovoltaics

A thesis presented in partial fulfilment of the requirements for the
degree of

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In

Chemistry

MASSEY UNIVERSITY
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For Mum, Dad and Huda

“anyone who has never made a mistake
has never tried anything new”

Albert Einstein, 1879-1955
theoretical physicist

Abstract

A designed series of novel boron-difluoride chelated aza-dipyrromethenes with particular physical properties have been synthesized for the purpose of exploring their usefulness as donors in organic photovoltaic (OPV) cells. Boron-difluoride chelated aza-dipyrromethenes are commonly referred in the literature as aza-BODIPYs, and this convention has been adopted in this thesis. The aza-BODIPYs synthesised were symmetrically substituted with aryl groups on the pyrrole rings. The synthesised aza-BODIPYs were: terthiophene-BF_2-aza-dipyrromethene (87), methoxy-terthiophene-BF_2-aza-dipyrromethene (88), triphenylamine-BF_2-aza-dipyrromethene (100), thiophene-triphenylamine-BF_2-aza-dipyrromethene (106), benzothiadiazole-BF_2-aza-dipyrromethene (111), benzothiadiazole-thiophene-BF_2-aza-dipyrromethene (112), benzothiadiazole-triphenylamine-BF_2-aza-dipyrromethene (113), ethylenedioxythiophene-BF_2-aza-dipyrromethene (125), thiophene-phenothiazine-BF_2-aza-dipyrromethene (132), thiophene-methylpyrrole-BF_2-aza-dipyrromethene (139), thiophene-carbazole-BF_2-aza-dipyrromethene (145), fluorenone-BF_2-aza-dipyrromethene (150), and thiophene-fluorenone-BF_2-aza-dipyrromethene (151). The numbers are used to refer to individual compounds in this thesis. Ruthenium dyes, terthiophene monomers and silicon quantum dots were also synthesised, again with a view to discovering novel donors for OPV cells.

The aza-BODIPYs were characterized spectroscopically by ultraviolet-visible (UV-VIS) absorption spectroscopy, fluorescence and time-correlated single-photon counting (TCSPC). Benzothiadiazole-triphenylamine-BF_2-aza-dipyrromethene (referred to as compound (113) in this thesis) was found to exhibit significant red-shifts in absorption (λ_{max}=855 nm) and emission (λ_{em}=953 nm). This compound showed a large bathochromic shift (205 nm) in absorption, in comparison with the standard BF_2-tetra-aryl aza-dipyrromethene (compound (4), λ_{max}=650 nm). Evidence has been found of strong intramolecular-charge-transfer (ICT) character in the excited state. It has been demonstrated how absorption and emission of aza-BODIPYs can be fine-tuned by manipulating the ICT between variously electronic donating and withdrawing substituents in the aza-BODIPY structure. Fluorescence and time-correlated single-photon counting (TCSPC) on the aza-BODIPYs in the presence of fullerenes supported the conclusion that there were charge transfer processes.

Time-dependent density functional theory (TD-DFT) has been successfully used to provide a guide to the structure-property relationships and electronic structures of the aza-BODIPYs. Absorption energies, calculated for the aza-BODIPYs using the B3LYP (Becke, three-parameter, Lee-Yang-Parr) exchange-correlation functional with a split-valence basis set of 6-311++G (2d, P). The B3LYP/6-311++G (2d, P) level of calculation delivered reasonable estimates of the absorption wavelengths for a number of the aza-BODIPYs, although the calculations did give poor estimates for the absorption wavelengths of others.

Photovoltaic devices were fabricated, using primarily carbon-60 fullerene as acceptor in conjunction with the aza-BODIPYs as donors, and successfully generated current on exposure to simulated solar radiation. Using a xenon arc lamp as a solar simulator, external photon-to-current quantum efficiencies (EQE) and overall power conversion efficiencies (η) were measured for these devices with a variety of layer structures, film compositions and film-processing conditions. Compound (106) and compound (113) gave EQEs of 3.89% and 3.01%, and overall power conversion efficiencies of 0.88% and 0.031% respectively. Current density-voltage (J-V) curves exhibit a significant inflection, which was reflected in the low fill factors (FF). The low values of EQE and η are attributed to low open-circuit voltage (V_{OC}) (0.32 V and 0.55 V in compounds (106) and (113)) and low fill factors (FF) (0.312 and 0.0147 in compounds (106) and (113)). The low V_{OC} and FF are possibly the result of an interfacial extraction barrier at one of the active layer interfaces, possibly between the active layer and the metal cathode. Avoiding the possibility of oxide and other layers through encapsulating the devices in an inert environment might remove the charge extraction barrier. The conclusion drawn is efficiencies of devices based on aza-BODIPYs might be improved significantly through further studies of interfaces and defects in devices.

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Abbreviations

ACN	acetonitrile
Ar	aromatic
$CDCl_3$	deuterated chloroform
conc	concentrated
Da	daltons
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	dichloromethane
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
DFT	density functional theory
DEA	Diethylamine
DIEA	*N*,*N*-Diisopropylethylamine
DME	Dimethyl ether
DMF	*N*,*N*-dimethylformamide
DSSC	dye sensitised solar cell
ESI	electrospray ionisation
EtOH	ethanol
FF	fill factor
ITO	indium tin oxide
J_{sc}	short circuit current
L	litres
LDA	Lithium diisopropylamide
MALDI	matrix assisted laser desorption ionisation
MeOH	methanol
min	minute
mL	millilitres
mmol	millimole
NBS	*N*-bromosuccinimide
NMP	N-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million
R_f	retention factor
TFA	Trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography

TMS	tetramethylsilane
TOF	time of flight
UV-Vis	ultraviolet-visible spectroscopy
V_{oc}	open circuit voltage