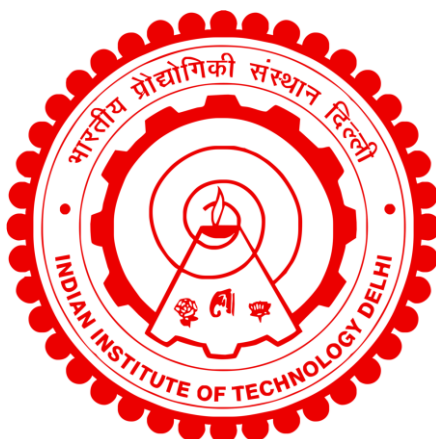


UNRAVELLING LOSS MECHANISMS IN NON-FULLERENE ORGANIC SOLAR CELLS: INTEGRATING DATA-DRIVEN MACHINE LEARNING AND EXPERIMENTAL APPROACHES

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INDIAN INSTITUTE OF TECHNOLOGY DELHI
SEPTEMBER 2024**

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Unravelling Loss Mechanisms in Non - Fullerene Organic Solar Cells: Integrating Data - Driven Machine Learning and Experimental Approaches

by

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Department of Energy Science and Engineering

Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy
to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

SEPTEMBER 2024

*Dedicated to
My Family...*

Certificate

This is to certify that the thesis entitled “**Unravelling Loss Mechanisms in Non-Fullerene Organic Solar Cells: Integrating Data-Driven Machine Learning and Experimental Approaches**”, submitted by **Mr. Rakesh Suthar** to the Indian Institute of Technology Delhi, India, for the award of the degree of **Doctor of Philosophy** is a record bonafide research work carried out by him under my supervision and guidance. He has fulfilled the requirements for the submission of the thesis, which to the best of my knowledge has reached the required standard. The material contained in the thesis has not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

Date: **27 Sept 2024**
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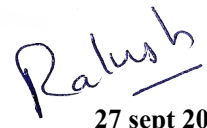
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27 sept 2024
Rakesh Suthar

Abstract

Over the last few years, organic solar cells (OSCs) have emerged as one of the most promising third-generation photovoltaic technologies due to unique advantages like low production costs, roll-to-roll solution processability, lightweight, and mechanical flexibility. Recent developments in novel conjugated polymer donor and non-fullerene acceptor (NFA) materials with promising properties have led to an unprecedented increase in power conversion efficiency (PCE) by more than 20%. Further improvement is still attainable with the optimal combinations of donors and acceptors that provide minimal voltage and current losses. However, in this era of artificial intelligence, identifying the highly potential combinations of such donor and acceptor materials using the current trial-and-error experimental approaches is certainly not feasible.

In this thesis, we explored the data-driven machine-learning (ML) framework for the analysis and prediction of photovoltaic parameters in non-fullerene organic solar cells and successively validated this predictivity by fabricating a set of highly efficient devices. Firstly, the data-enabled ML framework was employed to predict the energy losses using frontier molecular orbital (FMO) descriptors in the polymer:NFA-based devices. The Random Forest regression model showed the best performance in predicting the energy losses, with a correlation coefficient of 0.83 and a relative error in the range of 0–20%. We extended our work to predicting photovoltaic parameters (short circuit current density, open circuit voltage and PCE) using various combinations of FMO and RDKit descriptors and then validated the model by fabricating the devices. A dataset of 1242 experimentally verified donor:acceptor combinations was constructed, and the corresponding material descriptors were generated to train and test five different supervised ML models. Using a unique combination of both FMO and RDKit descriptors as input features, the random forest ML model performed best for

predicting the PCE with a Person's coefficient of 0.791 and a mean absolute percentage error of 2.004. Furthermore, the importance of critical RDKit descriptors along with FMO descriptors in such performance predictions was realized by SHapley Additive exPlanations (SHAP) analyses. Therefore, these new descriptors will guide the proposed ML framework, which will be beneficial for designing new molecules, screening, and predicting suitable donor:acceptor combinations, thereby accelerating the development of highly efficient OSCs.

In addition to the donor:acceptor virtual screening and performance predication, OSCs still have a large open circuit voltage loss ($\Delta V_{OC} \sim 0.6$ V) because of molecular disorder and high energetic offsets, as well as photocurrent losses because of the excitonic nature of photoactive layer. For this, we explored how exciton lifetime, energetic offsets, and disorder affect the voltage loss in bulk heterojunction organic solar cells. This has enabled us to identify the key features for minimizing the voltage loss, like (1) a low energy offset between the donor and acceptor molecular states is essential to attain a non-radiative voltage loss as low as ~ 200 meV and (2) Urbach energy, which is a measure of the materials' disorder and packing, should be low for the minimization of the radiative voltage loss.

On the other hand, the photocurrent losses were reduced by utilizing the synergistic plasmonic effects of multi-shaped Au nanostructures (diameter/edge length ~ 50 nm) hybridized with few-layer WS_2 nanosheets to improve the photocurrent of fullerene and non-fullerene-based OSCs. A PCE enhancement of more than 15% and an external quantum efficiency improvement in a broad wavelength range of 350-700 nm were demonstrated by incorporating these Au- WS_2 nanohybrids as an interlayer between hole-transport and photoactive layers. The effective plasmonic range over 350–700 nm and more than 50% forward light scattering indicated that these hybridized Au nanostructures are highly suitable candidates to couple the incident light into the active layer. Near field intensity enhancement and subsequent enhancement in absorption density confirmed the elevated local density of

optical states in Au-WS₂ nanohybrid-based devices. Therefore, the present study emphasizes the role of hybridized Au-WS₂ nanostructures in improving the light-harvesting capability of OSCs in a broad wavelength range, thereby attaining a significant improvement in device photocurrent. Overall, this thesis helps to screen the potential donor:acceptor combination and how to reduce photovoltage and photocurrent losses in OSCs for its successful commercialization.

पिछले कुछ वर्षों में, कम उत्पादन लागत, रोल-टू-रोल समाधान प्रक्रियाशीलता, हल्के वजन और यांत्रिक लचीलेपन जैसे अद्वितीय लाभों के कारण कार्बनिक सौर सेल (ओएससी), तीसरी पीढ़ी की सबसे आशाजनक फोटोवोल्टिक प्रौद्योगिकियों में से एक के रूप में उभरे हैं। आशाजनक गुणों वाले नवीन संयुग्मित पॉलिमर दाता और गैर-फुलरीन स्वीकर्ता (एनएफए) सामग्रियों में हाल के विकास से बिजली रूपांतरण दक्षता (पीसीई) में 20% से अधिक की अभूतपूर्व वृद्धि हुई है। दाताओं और स्वीकर्ता के इष्टतम संयोजन के साथ और सुधार अभी भी प्राप्य है जो न्यूनतम फोटोवोल्टेज और फोटोकॉरंट हानि प्रदान करता है। हालाँकि, कृत्रिम बुद्धिमत्ता के इस युग में, वर्तमान परीक्षण-और-त्रुटि प्रयोगात्मक दृष्टिकोण का उपयोग करके ऐसे दाता और स्वीकर्ता सामग्रियों के अत्यधिक संभावित संयोजनों की पहचान करना निश्चित रूप से संभव नहीं है।

इस थीसिस में, हमने गैर-फुलरीन कार्बनिक सौर सेल में फोटोवोल्टिक मापदंडों के विश्लेषण और भविष्यवाणी के लिए डेटा-संचालित मशीन-लर्निंग ढांचे की खोज की और अत्यधिक कुशल कार्बनिक सौर सेल का एक सेट बनाकर इस भविष्यवाणी को क्रमिक रूप से मान्य किया। सबसे पहले, डेटा-सक्षम एमएल फ्रेमवर्क को पॉलिमर: गैर-फुलरीन स्वीकर्ता-आधारित सौर सेल में फ्रंटियर आणविक कक्षीय (FMO) डिस्क्रिप्टर का उपयोग करके ऊर्जा हानि की भविष्यवाणी करने के लिए नियोजित किया गया था। जिसमें रैंडम फ़ॉरेस्ट रिग्रेशन मॉडल ने 0.83 के सहसंबंध गुणांक और 0-20% की सीमा में सापेक्ष त्रुटि के साथ, ऊर्जा हानि की भविष्यवाणी करने में सबसे अच्छा प्रदर्शन दिखाया। हमने FMO और RDKit डिस्क्रिप्टर के विभिन्न संयोजनों का उपयोग करके फोटोवोल्टिक मापदंडों (शॉर्ट सर्किट वर्तमान घनत्व, ओपन सर्किट वोल्टेज और पीसीई) की भविष्यवाणी करने के लिए अपना काम बढ़ाया और फिर कार्बनिक सौर सेल का निर्माण करके मॉडल को मान्य किया। 1242 प्रयोगात्मक रूप से सत्यापित दाता: स्वीकर्ता संयोजनों का एक डेटासेट बनाया गया था, और पांच अलग-अलग पर्यवेक्षित एमएल मॉडल को प्रशिक्षित और परीक्षण करने के लिए संबंधित सामग्री विवरणक उत्पन्न किए गए थे। इनपुट सुविधाओं के रूप में एफएमओ और RDKit डिस्क्रिप्टर दोनों के एक अद्वितीय संयोजन का उपयोग करते हुए, रैंडम फ़ॉरेस्ट एमएल मॉडल ने 0.791 के सहसंबंध गुणांक और 2.004 की औसत पूर्ण प्रतिशत त्रुटि के साथ पीसीई की भविष्यवाणी करने के लिए सबसे अच्छा प्रदर्शन किया। इसके अलावा, ऐसे प्रदर्शन पूर्वानुमानों में FMO डिस्क्रिप्टरों के साथ-साथ महत्वपूर्ण RDKit डिस्क्रिप्टरों के महत्व को SHapley Additive exPlanations (SHAP) विश्लेषणों द्वारा समझा गया था। अतः, ये नए डिस्क्रिप्टर प्रस्तावित एमएल ढांचे का मार्गदर्शन

करेंगे, जो नए अणुओं को डिजाइन करने, स्क्रीनिंग और उपयुक्त डी/ए संयोजनों की भविष्यवाणी करने के लिए फायदेमंद होगा, जिससे अत्यधिक कुशल ओएससी के विकास में तेजी आएगी।

दाता-स्वीकर्ता वर्चुअल स्क्रीनिंग और फोटोवोल्टिक पैरामीटर भविष्यवाणी के अलावा, आणविक विकार और उच्च ऊर्जावान ऑफसेट के कारण ओएससी में अभी भी एक बड़ा ओपन सर्किट वोल्टेज नुकसान (~ 0.6 V) है, साथ ही फोटोएक्टिव परत की एक्साइटोनिक प्रकृति के कारण फोटोकॉरंट नुकसान भी है। इसके लिए, हमने पता लगाया कि कैसे एक्साइटन जीवनकाल, ऊर्जावान ऑफसेट और विकार हेटेरोजंक्शन कार्बनिक सौर सेल में वोल्टेज हानि को प्रभावित करते हैं। इसने हमें वोल्टेज हानि को कम करने के लिए प्रमुख विशेषताओं की पहचान करने में सक्षम बनाया है, जैसे (1) गैर-विकिरण वोल्टेज हानि प्राप्त करने के लिए दाता और स्वीकर्ता आणविक राज्यों के बीच कम ऊर्जा ऑफसेट आवश्यक है जोकि कम से कम ~ 200 meV है, और (2) उरबैच ऊर्जा, जो सामग्री के विकार और पैकिंग का एक माप है, विकिरण वोल्टेज हानि को कम करने के लिए कम होनी चाहिए।

दूसरी ओर, फुलरीन और गैर-फुलरीन-आधारित के फोटोकॉरंट को बेहतर बनाने के लिए कुछ-परत WS_2 नैनोशीट्स के साथ संकरणित बहु-आकार वाले Au नैनोस्ट्रक्चर (व्यास / किनारे की लंबाई ~ 50 nm) के सहक्रियात्मक प्लास्मोनिक प्रभावों का उपयोग करके फोटोकॉरंट हानि को कम किया गया था। ओएससी. छेद-परिवहन और फोटोएक्टिव परतों के बीच एक इंटरलेयर के रूप में इन Au- WS_2 नैनोहाइब्रिड्स को शामिल करके 15% से अधिक की पीसीई वृद्धि और 350-700 nm की व्यापक तरंग दैर्ध्य रेंज में बाहरी क्वांटम दक्षता में सुधार का प्रदर्शन किया गया। 350-700 nm से अधिक प्रभावी प्लास्मोनिक रेंज और 50% से अधिक आगे प्रकाश बिखरने से संकेत मिलता है कि ये संकरित एयू नैनोस्ट्रक्चर सक्रिय परत में घटना प्रकाश को जोड़ने के लिए अत्यधिक उपयुक्त उम्मीदवार हैं। निकटवर्ती क्षेत्र की तीव्रता में वृद्धि और उसके बाद अवशोषण घनत्व में वृद्धि ने Au- WS_2 नैनोहाइब्रिड-आधारित उपकरणों में ऑप्टिकल राज्यों के ऊंचे स्थानीय घनत्व की पुष्टि की। इसलिए, वर्तमान अध्ययन व्यापक तरंग दैर्ध्य रेंज में ओएससी की प्रकाश-संचयन क्षमता में सुधार करने में हाइब्रिडाइज्ड Au- WS_2 नैनोस्ट्रक्चर की भूमिका पर जोर देता है, जिससे डिवाइस फोटोकॉरंट में महत्वपूर्ण सुधार प्राप्त होता है। कुल मिलाकर, यह थीसिस संभावित दाता: स्वीकर्ता संयोजन की जांच करने में मदद करती है और उनके सफल व्यावसायीकरण के लिए ओपीवी उपकरणों में फोटोवोल्टेज और फोटोकॉरंट नुकसान को कैसे कम किया जाए।

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List of abbreviations and symbols

OSC	Organic Solar Cell
NREL	National Renewable Energy Laboratory
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
D/A	Donor-Acceptor
NFA	Non-Fullerene Acceptors
ML	Machine Learning
SQ	Shockley–Queisser
PL	Photoluminescence
TRPL	Time Resolved Photoluminescence
FE-SEM	Field-Emission Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
FMO	Frontier Molecular Orbitals
LDOS	Local Density of Optical States
QSAR	Quantitative Structure-Activity Relationships
DFT	Density Functional Theory
DT / DTR	Decision Tree Regression
SVM	Support Vector Machine Regression
GB / GBR	Gradient Boosting Regression
RF	Random Forest Regression
ANN	Artificial Neural Network Regression
XGBoost	eXtreme Gradient Boosting regression
MAPE	Mean Absolute Percentage Error
RMSE	Root Mean Squared Error
C-V	Cross-Validation
SHAP	SHapley Additive exPlanations
SMILES	Simplified Molecular Input Line Entry System
ZnO	Zinc Oxide
MoO _x	Molybdenum Oxide
Au	Gold

WS ₂	Tungsten Disulfide
Au-WS ₂	Gold - Tungsten Disulfide Nanohybrid
LiF	Lithium Fluoride
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PFN-Br	Poly(9,9-bis(3'-(N,N-dimethyl)-N-ethylammonium-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene))dibromide
P3HT	Poly(3-hexylthiophene-2,5-diyl)
PTB7	Poly [[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]
PTB7-Th	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-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2,6-diyl)]
PBDB-T	Poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione))]
PM6	Poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione))]
PCBM(PC ₇₁ BM)	[6,6]-Phenyl-C71-butyric acid methyl ester
ITIC	(5Z)-3-ethyl-2-sulfanylidene-5-[[4-[9,9,18,18-tetrakis(2-ethylhexyl)-15-[7-[(Z)-(3-ethyl-4-oxo-2-sulfanylidene-1,3-thiazolidin-5-ylidene)methyl]-2,1,3-benzothiadiazol-4-yl]-5,14-dithiapentacyclo[10.6.0.0.3,101(12),2,4(8),6,10,13(17),15-heptaen-6-yl]-2,1,3-benzothiadiazol-7-yl]methylidene]-1,3-thiazolidin-4-one
IT-4F	3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene
Y6	2,2'-[[12,13-Bis(2-butyloctyl)-12,13-dihydro-3,9-dinonylbisthieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-e:2'',3'-

	g][2,1,3]benzothiadiazole-2,10-diyl]bis[methyldiylidyne(5,6-chloro-3-oxo-1H-indene-2,1(3H)-diylidene)]bis[propanedinitrile]
BTP-eC9	2,2'- [[12,13-Bis(2-butyloctyl)-12,13-dihydro-3,9-dinonylbisthieno[2'',3'':4',5']thieno[2',3':4,5]pyrro:2',3'-g][2,1,3]benzothiadiazole-2,10-diyl]bis[methyldiylidyne(5,6-chloro-3-oxo-1H-indene-2,1(3H)-diylidene)]]bis[propanedinitrile]
$\Delta E_{\text{LUMO}} / \Delta E_{\text{LUMO}}$	LUMO-LUMO offset
$\Delta E_{\text{HOMO}} / \Delta E_{\text{HOMO}}$	HOMO-HOMO offset
$E_{\text{g,min}}$	Bandgap of the Active Layer
E_{g}	Bandgap of the Materials
P_{in}	Input Power
PCE	Power Conversion Efficiency
J_{SC}	Short-circuit Current Density
V_{OC}	Open-circuit Voltage
FF	Fill Factor
q	Elementary Charge
$V_{\text{OC,SQ}}$	Maximum achievable V_{OC} by SQ limit
$V_{\text{OC,rad}}$	Maximum achievable V_{OC} by radiative limit
$J_{\text{SC,SQ}}$	Maximum achievable J_{SC} by SQ limit
$\Delta V_{\text{OC,rad}}$	Radiative Voltage Loss
$\Delta V_{\text{OC,nrad}}$	Non-radiative Voltage Loss
ΔV_{OC}	Total Voltage Loss
$k_{\text{B}}T$	Room Temperature Thermal Energy
E_{U}	Urbach Energy
$\Delta\omega$	Wavenumber Difference
n	Total Number of Data
x_i	Experimental Value
y_i	Predicted Value
$\bar{x}$	Average of Experimental Value
$\bar{y}$	Average of Predicted Value
r	Pearson's Correlation Coefficient

σ_{abs}	Absorption Cross-Section
σ_{scat}	Scattering Cross-Section
Q_s	Relative Scattering Efficiency