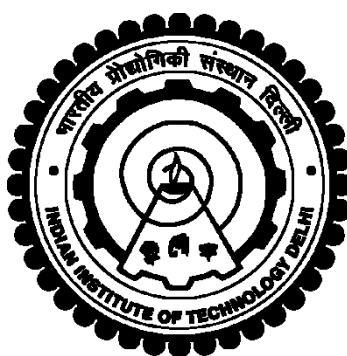


**PERYLENE DIIMIDE AND AZO BASED CONJUGATED  
POLYMERS: SYNTHESIS AND APPLICATIONS TO  
ORGANIC PHOTOVOLTAICS**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI  
OCTOBER 2019**

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ORGANIC PHOTOVOLTAICS**

by

**SAVITA MEENA**

Department of Materials Science and Engineering

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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## CERTIFICATE

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This is to certify that the thesis entitled "**Perylene Diimide and Azo based Conjugated Polymers: Synthesis and Applications to Organic Photovoltaics**" being submitted by **Ms. Savita Meena** to the Indian Institute of Technology Delhi New Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. **Ms. Savita Meena** has worked under my guidance and supervision and has fulfilled the requirements for the submission of her thesis, which to our knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any University or Institute for the award of any other degree or diploma.

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**SAVITA MEENA**

## ABSTRACT

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Research in the field of low band gap conjugated polymers is of current interest with increase in the need to develop cost efficient sustainable energy sources. These materials are having great significance owing to wide range of potential applications in the field of optoelectronic devices. The most plausible method to design low band gap conjugated polymers is the D-A approach where an electron rich moiety alternates with an electron deficient moiety in a D-A copolymer. The most commonly known D-A units are perylene diimide derivatives, fluorene, carbazole, cyclopentadithiophene, benzothiadiazole, thiophene etc Copolymers based on perylene diimide and aromatic azo linkage with different functionalities are immensely important and useful because of their high charge carrier mobilities and facile tunability of their absorption bands.

The present thesis is mainly focused on the design and synthesis of perylene diimide and azo linkage based monomers. These monomers were copolymerized with different D-A moieties to develop a series of novel polymers and their potential for use in photovoltaic device applications were evaluated. A precursor approach has been adopted in this work to synthesize various difunctional monomers with bromine atoms at the desired positions for coupling, thereby avoiding non-selective bromination. Herein, all the polymers were synthesized using traditional carbon-carbon coupling methods such as Suzuki and direct arylation polymerization reactions.

In the first Chapter, introduction and literature survey including an overview of  $\pi$ -conjugated polymers have been presented.

In the second Chapter, synthesis and characterization of a series of new dioctylfluorene extended N-substituted perylene diimide based D-A type alternating copolymers and their photovoltaic device studies are presented. 2,9-Bis(7-bromo-9,9-dioctyl-

9*H*-fluoren-2-yl)anthra[2,1,9-def:6,5,10-*d'ef'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetrone **M6** was synthesized using a facile synthetic approach by the condensation reaction of **M4** with **M5**. Polymers **P1-P3** were synthesized by Suzuki polymerization whereas **P4-P6** by direct arylation polymerization reactions of **M6** with different D-A units. All the copolymers exhibited good thermal stability and solubility in all chlorinated solvents. **P1-P6** showed broad absorption spectra in solution as well as in thin film where  $\lambda_{\max}$  range from 300 to 954 nm extended upto near infrared region with narrow  $E_g^{\text{opt}}$  in range of 1.17 to 2.08 eV. Polymers exhibit suitably aligned HOMO-LUMO energy levels for blending with P3HT or perovskite to fabricate BHJ or perovskite solar cell devices. BHJ device of **P5**:P3HT blend film in 1:1 weight ratio shows the best PCE upto 1.96%. **P3** and **P4** were used in perovskite solar cell devices as HTMs and achieved PCEs of 13.02% and 10.74%, respectively.

In the third Chapter, a series of novel fluorene based conjugated polymers **P7-P13** containing azo linkage as a part of the main polymeric backbone were synthesized and characterized. A simple and efficient synthetic routes i.e. oxidative coupling and borylation reaction, respectively were used to synthesize azo linkage based target monomers 1,2-bis(7-bromo-9,9-dioctyl-9*H*-fluoren-2-yl)diazene **M18** and 1,2-bis(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluoren-2-yl)diazene **M19**. Both the monomers were copolymerized with different D-A units to obtain polymers **P7-P13** either by Suzuki or direct arylation polymerization reactions. All the polymers possess good thermal stability with  $T_5$  greater than 300 °C. The polymers synthesized by direct arylation method exhibited good molecular weight  $M_w$  of upto 44.60 Kg mol<sup>-1</sup>. All polymers displayed broad absorption spectra in solution and in thin film where  $\lambda_{\max}$  ranging from 437 to 532 nm with narrow  $E_g^{\text{opt}}$  in range of 1.81 to 2.35 eV. The main chain azo linkage polymers **P12** and **P13** exhibit HOMO energy levels of -5.88 and -5.39 eV, respectively found ideally matched with

HOMO levels of C71-PCBM therefore used for OPV device fabrications. OPV device based on **P13**:C71-PCBM blend film in 1:2 weight ratio exhibited the best PCE of 0.53%.

In the fourth Chapter, the synthesis and characterization of novel side chain azo linkage conjugated polymers **P14-P19** are presented. A more comprehensive diazotization coupling method with precursor approach was adopted to design the bifunctional azo linkage target monomers 4-((2,5-dibromophenyl)diazenyl)-N,N-dimethylaniline **M26**, 4,4'-((4,4'-dibromo-[1,1'-biphenyl]-2,2'-diyl)bis(diazene-2,1-diyl))bis(N,N-dimethylaniline) **M30** and their octyl analogues **M27** and **M31** featuring one or two characteristic azo linkages. **M27** was copolymerized with different D-A type co-monomers to synthesize polymers **P14-P19**. The copolymers **P14-P16** were synthesized by Suzuki polymerization whereas **P17-P19** by direct arylation polymerization reactions. All polymers have good molecular weight  $M_w$  ranged from 9.31 to 14.56 Kg mol<sup>-1</sup> and thermal stability  $T_5$  in range of 222 to 338 °C. **P14-P19** exhibit broad absorption maxima in solution and thin film ranging from 417 to 546 nm. The band gaps i.e.  $E_g^{opt}$  and  $E_g^{elec}$  of all polymers were ranged from 1.78-2.33 and 1.51-1.83 eV, respectively. **P15** and **P18** were blended with C71-PCBM in 1:2 weight ratio to fabricate OPV devices. OPV device based on **P18**:C71-PCBM blend films exhibited the best PCE upto 0.11%. **P15** polymer was used in perovskite solar cell as HTM and achieved PCE of 12.80%. The side chain azo linkage polymers are found to be promising for OPV applications as well as for use as HTM in perovskite solar cell.

Overall, a simple, cost-effective and environment friendly method such as DArP was used to develop low band gap conjugated polymers with high molecular weight for photovoltaic applications. Solubility of these high molecular weight conjugated polymers in common organic solvents always remains a problem that has been successfully overcome by incorporating long octyl chain substituted functionalities in the polymer backbone, as they are promising to improve solubility.

## सार

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कम बैंड गैप संयुग्मित पॉलिमर के क्षेत्र में अनुसंधान लागत कुशल टिकाऊ ऊर्जा स्रोतों को विकसित करने की आवश्यकता में वृद्धि के साथ वर्तमान रुचि है। ये सामग्री ऑप्टोइलेक्ट्रॉनिक उपकरणों के क्षेत्र में संभावित अनुप्रयोगों की विस्तृत श्रृंखला के कारण बहुत महत्व रखती हैं। कम बैंड गैप संयुग्मित पॉलिमर डिजाइन करने के लिए सबसे प्रशंसनीय विधि डी-ए दृष्टिकोण है जहां एक डी-ए कोपॉलीमर में एक इलेक्ट्रॉन की कमी वाले मोइटी के साथ एक इलेक्ट्रॉन समृद्ध मोइटी वैकल्पिक होता है। सबसे अधिक ज्ञात डी-ए इकाइयाँ पेरिलीन डाईमाइड डेरिवेटिव, फ्लुरीन, कार्बाज़ोल, साइक्लोपेंटाडाइथायोफीन, बेंजाथायडाज़ोल, थायोफीन आदि हैं। विभिन्न कार्यात्मकताओं के साथ पेरिलीन डाइमाइड और एरोमैटिक एज़ो लिंकेज पर आधारित कॉपोलिमर उनके उच्च चार्ज वाहक गतिशीलता और उनके अवशोषण बैंड की सुस्पष्टता के कारण काफी महत्वपूर्ण और उपयोगी होते हैं।

वर्तमान थीसिस मुख्य रूप से पेरिलीन डाईमाइड और एज़ो लिंकेज आधारित मोनोमर्स के डिजाइन और संश्लेषण पर केंद्रित है। इन मोनोमर्स को नोवल पॉलिमर की एक श्रृंखला को विकसित करने के लिए अलग-अलग डी-ए मोइटी के साथ कोपॉलीमेराइज्ड किया गया था और फोटोवोल्टिक डिवाइस अनुप्रयोगों में उपयोग की उनकी क्षमता का मूल्यांकन किया गया था। युग्मन के लिए वांछित पदों पर ब्रोमीन परमाणुओं के साथ विभिन्न विशिष्ट मोनोमर्स को संश्लेषित करने के लिए इस कार्य में एक अग्रदूत दृष्टिकोण अपनाया गया है, जिससे गैर-चयनात्मक ब्रोमिनेशन से बचा जा सके। इसमें, सभी पॉलिमर को सुजुकी और प्रत्यक्ष अराईलेएशन पोलिमेराइजेशन प्रतिक्रियाओं जैसे पारंपरिक कार्बन-कार्बन युग्मन विधियों का उपयोग करके संश्लेषित किया गया था।

पहले अध्याय में,  $\pi$ -संयुग्मित पॉलिमर का अवलोकन सहित परिचय और साहित्य सर्वेक्षण प्रस्तुत किया गया है।

दूसरे अध्याय में, एक नई श्रृंखला जोकि डाईओक्टाईलफ्लुरीन विस्तारित एन-प्रतिस्थापित पेरिलीन डाईमाइड पर आधारित डी-ए प्रकार अल्टरनेटिंग कॉपोलिमर के संश्लेषण, लक्षण एवम उनके फोटोवोल्टिक डिवाइस अध्ययन वर्णन को प्रस्तुत किया गया है। 2,9-Bis(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)anthra[2,1,9-def:6,5,10-d'e'f]diisoquinoline-1,3,8,10(2H,9H)-tetrone **M6** को **M5** के साथ **M4** की संक्षेपण प्रतिक्रिया द्वारा एक सुस्पष्ट सिंथेटिक दृष्टिकोण का उपयोग करके संश्लेषित किया गया था।

पॉलिमर **P1-P3** को सुजुकी पोलीमराइजेशन द्वारा संश्लेषित किया गया था जबकि **P4-P6** अलग-अलग डी-ए इकाइयों के साथ **M6** के प्रत्यक्ष अराईलेेशन पोलीमराइजेशन प्रतिक्रिया द्वारा। सभी कोपोलिमर्स ने सभी क्लोरीनयुक्त सॉल्वेंट्स में अच्छी थर्मल स्थिरता और घुलनशीलता का प्रदर्शन किया। **P1-P6** ने घोल में और साथ ही पतली फिल्म में व्यापक अवशोषण स्पेक्ट्रा दिखाया, जहां  $\lambda_{\max}$  300 से 954 nm तक संकीर्ण  $E_g^{\text{opt}}$  1.17 से 2.08 eV की सीमा के साथ अवरक्त क्षेत्र के पास बढ़ाया गया। पॉलिमर BHJ या पेरोस्काइट सौर सेल उपकरणों को बनाने के लिए P3HT या पेरोस्काइट के साथ सम्मिश्रण के लिए उपयुक्त रूप से HOMO-LUMO ऊर्जा स्तरों को प्रदर्शित करता है। **P5:P3HT** ब्लेंड फिल्म 1: 1 के वजन अनुपात का BHJ डिवाइस 1.96% तक का सर्वश्रेष्ठ PCE दिखाता है। **P3** और **P4** को HTM के रूप में पेरोस्काइट सौर सेल उपकरणों में इस्तेमाल किया गया था और क्रमशः 13.02% और 10.74% का PCE हासिल किया।

तीसरे अध्याय में, मुख्य पोलीमरिक बेकबोन के एक भाग के रूप में एज़ो लिंकेज वाले नोवल फ्लुरीन आधारित संयुग्मित पॉलिमर **P7-P13** की एक श्रृंखला को संश्लेषित किया गया था। एक सरल और कुशल सिंथेटिक मार्ग यानी ऑक्सीडेटिव युग्मन और बोराइलिएशन प्रतिक्रिया, क्रमशः एज़ो लिंकेज आधारित लक्ष्य मोनोमर्स 1,2-bis(7-bromo-9,9-dioctyl-9H-fluoren-2-yl)diazene **M18** और 1,2-bis(9,9-dioctyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluoren-2-yl)diazene **M19** संश्लेषित करने के लिए उपयोग किया गया था। सुजुकी या प्रत्यक्ष अराईलेेशन पोलीमराइजेशन प्रतिक्रियाओं द्वारा पॉलिमर **P7-P13** प्राप्त करने के लिये दोनों मोनोमर्स को अलग-अलग डी-ए इकाइयों के साथ कोपॉलीमराइज्ड किया गया था। सभी पॉलिमर  $T_5$  के साथ 300 °C से अधिक अच्छी तापीय स्थिरता रखते हैं। प्रत्यक्ष अराईलेेशन पोलीमराइजेशन विधि द्वारा संश्लेषित पॉलिमर ने 44.60 किलोग्राम प्रति मोल तक के अच्छे आणविक भार  $M_w$  का प्रदर्शन किया। सभी पॉलिमर ने घोल में व्यापक अवशोषण स्पेक्ट्रा प्रदर्शित किया और पतली फिल्म में जहां  $\lambda_{\max}$  437 से 532 nm संकीर्ण  $E_g^{\text{opt}}$  के साथ 1.81 से 2.35 eV की सीमा में है। क्रमशः मुख्य श्रृंखला एज़ो लिंकेज पॉलिमर **P12** और **P13** के HOMO ऊर्जा स्तर -5.88 और -5.39 eV प्रदर्शित हुये हैं, जोकि क्रमशः आदर्श रूप से C71-PCBM के HOMO स्तरों के साथ मेल खाते हैं इसलिए OPV निर्माण के लिए इन्हें उपयोग किया गया है। **P13:C71-PCBM** मिश्रण फिल्म 1:2 के वजन अनुपात पर आधारित OPV डिवाइस में सबसे अच्छा PCE 0.53% प्रदर्शित किया गया।

चौथे अध्याय में, नोवल पक्ष श्रृंखला एज़ो लिंकेज संयुग्मित पॉलिमर **P14-P19** के संश्लेषण और लक्षण वर्णन प्रस्तुत किए गए हैं। अग्रदूत दृष्टिकोण के साथ अधिक व्यापक डायएज़ोटाइज़ेशन युग्मन विधि द्वारा द्विपद एज़ो लिंकेज लक्ष्य मोनोमर्स 4-((2,5-dibromophenyl)diazanyl)-N,N-dimethylaniline **M26**, 4,4'-((4,4'-dibromo-[1,1'-biphenyl]-2,2'-diyl)bis(diazene-2,1-diyl))bis(N,N-dimethylaniline) **M30** और उनके ऑक्टाइल एनालॉग्स **M27** और **M31** जोकि एक या दो एज़ो लिंकेज की विशेषता के साथ संश्लेषित किये गये हैं। **M27** पॉलिमर **P14-P19** को संश्लेषित करने के लिए विभिन्न डी-ए प्रकार के कोमोनोमर्स के साथ कोपॉलीमेराइज़्ड किया गया था। कोपॉलिमर्स **P14-P16** को सुजुकी पोलिमेराइज़ेशन द्वारा जबकि **P17-P19** को प्रत्यक्ष अराईलेेशन पोलिमेराइज़ेशन प्रतिक्रियाओं द्वारा संश्लेषित किया गया है। सभी पॉलिमर में आणविक भार  $M_w$  9.32 से लेकर 14.56 किलोग्राम प्रति मोल और थर्मल स्थिरता  $T_5$  222 से 338 °C तक जोकि अच्छा है। **P14-P19** घोल और पतली फिल्म में व्यापक अवशोषण मैक्सिमा 417 से 546 nm तक प्रदर्शित करते हैं। सभी पॉलिमर के बैंड गैप यानी  $E_g^{opt}$  और  $E_g^{elec}$  क्रमशः 1.78-2.33 और 1.51-1.83 eV से लेकर थे। **P15** और **P18** को OPV डिवाइसों को बनाने के लिए 1:2 भार अनुपात में C71-PCBM के साथ मिश्रित किया गया था। **P18**:C71-PCBM मिश्रण फिल्मों पर आधारित OPV डिवाइस ने 0.11% तक का सर्वश्रेष्ठ PCE प्रदर्शित किया। **P15** पॉलिमर का HTM के रूप में पेरोस्काइट सोलर सेल में उपयोग किया गया और 12.80% का PCE हासिल किया। पक्ष श्रृंखला एज़ो लिंकेज पॉलिमर को OPV अनुप्रयोगों के लिए और साथ ही पेरोस्काइट सोलर सेल में HTM के रूप में उपयोग के लिए आशाजनक पाया जाता है।

कुल मिलाकर, DA<sub>r</sub>P जैसे एक सरल, लागत प्रभावी और पर्यावरण के अनुकूल विधि का उपयोग उच्च आणविक भार के साथ कम बैंड गैप संयुग्मित पॉलिमर को फोटोवोल्टिक अनुप्रयोगों के लिए विकसित किया गया था। आम कार्बनिक विलियानो में इन उच्च आणविक भार संयुग्मित पॉलिमर की विलेयता हमेशा एक समस्या बनी हुई है जिसे बहुलक बैकबोन में लंबी ऑक्टाइल श्रृंखला प्रतिस्थापित कार्यात्मकताओं को शामिल करके सफलतापूर्वक दूर किया गया है, क्योंकि वे घुलनशीलता में सुधार करने का वादा कर रहे हैं।

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## GLOSSARY OF SYMBOLS AND ABBREVIATIONS

---

|              |                   |
|--------------|-------------------|
| %            | Percent           |
| $\delta$     | Chemical shift    |
| s            | Singlet           |
| d            | Doublet           |
| dd           | Double doublet    |
| t            | Triplet           |
| m            | Multiplet         |
| br           | Broad signal      |
| vs           | Versus            |
| cm           | Centimeter        |
| nm           | Nanometer         |
| g            | Gram              |
| mg           | Milligram         |
| mol          | Mole              |
| mmol         | Millimole         |
| L            | Litre             |
| mL           | Millilitre        |
| $\mu$ L      | Microlitre        |
| ppm          | Part per million  |
| $^{\circ}$ C | Degree centigrade |
| h            | Hour              |
| Min.         | Minute            |
| $\nu$        | Frequency         |

|                     |   |
|---------------------|---|
| Hz                  | Hertz   |
| MHz                 | Megahertz                                     |
| $\lambda_{\max}$    | Absorption maximum                            |
| $T_5$               | Decomposition temperature at 5% weight loss   |
| e.g.                | For example                                   |
| i.e.                | That is                                       |
| $D$                 | Dispersity                                    |
| $M_w$               | Weight average molecular weight               |
| $M_n$               | Number average molecular weight               |
| Aliquat336          | Trioctylmethylammonium chloride               |
| AFM                 | Atomic force microscopy                       |
| BHJ                 | Bulk heterojunction                           |
| C71-PCBM            | Phenyl-C71-butyric acid methyl ester          |
| DMF                 | Dimethylformamide                             |
| D-A                 | Donor-acceptor                                |
| DArP                | Direct arylation polymerization               |
| DSC                 | Differential scanning calorimetry             |
| DCB                 | 1,2-Dichlorobenzene                           |
| $E_g^{\text{opt}}$  | Optical band gap                              |
| $E_g^{\text{elec}}$ | Electrochemical band gap                      |
| EQE                 | External quantum efficiency                   |
| ETM                 | Electron transporting material                |
| Exciton             | Electron-hole pair                            |
| FT-IR               | Fourier transform infrared spectroscopy       |
| F8BT                | Poly(9,9'-dioctylfluorene-co-benzothiadazole) |

|              |  |
|--------------|--|
| GPC          | Gel permeation chromatography  |
| CV           | Cyclic voltammetry   |
| HTM          | Hole transporting material   |
| HOMO         | Highest occupied molecular orbital   |
| ICT          | Internal charge transfer   |
| ITO          | Indium tin oxide   |
| J-V          | Current density-voltage  |
| LUMO         | Lowest unoccupied molecular orbital  |
| Li-TFSI      | lithium bis(trifluoromethanesulfonyl)-imide                                  |
| MDMO-PPV     | Poly(2-methoxy-5-(3,7-dimethyloctyloxy))-1,4-phenylenevinylene               |
| MALDI-TOF MS | Matrix-assisted laser desorption/Ionization time of flight mass spectrometry |
| n-BuLi       | Normal-butyllithium  |
| NaOH         | Sodium hydroxide   |
| NBS          | N-bromosuccinimide   |
| NMR          | Nuclear magnetic resonance   |
| NMP          | N-Methylpyrrolidone  |
| OFETs        | Organic field effect transistors   |
| OLEDs        | Organic light emitting diodes  |
| OPV          | Organic photovoltaic   |
| OSCs         | Organic solar cells  |
| P3HT         | poly(3-hexylthiophene-2,5-diyl)  |
| PCz          | poly(carbazole)  |
| PTC          | Phase transfer catalyst  |

|              |   |
|--------------|---|
| PDI          | Perylene-3,4,9,10-tetracarboxylicdiimide  |
| PFB          | Poly(9,9'-dioctylfluorene-co-bis-N,N-(4-butylphenyl)-bis-N,N-phenyl-1,4 phenylenediamine                        |
| PL           | Photoluminescence   |
| PEDOT:PSS    | Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)   |
| PCE          | Power conversion efficiency   |
| Spiro-OMeTAD | 2,2',7,7'-Tetrakis(N,N-di-p-methoxyphenylamino)-9,9'-spirobifluorene  |
| tBP          | 4-Tert-butylpyridine  |
| FK209        | Tris(2-(1 <i>H</i> -pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III)tris(bis(trifluorouoromethylsulfonyl)-imide) |
| TBAB         | Tetrabutylammonium bromide  |
| TBAP         | Tetrabutylammonium perchlorate  |
| TBAOH        | Tetrabutylammonium hydroxide  |
| TBTT         | Thiophene benzothiadiazole thiophene  |
| TGA          | Thermogravimetric analysis  |
| THF          | Tetrahydrofuran   |
| TMS          | Tetramethylsilane   |
| UV-Vis       | Ultraviolet-visible   |
| $V_{oc}$     | Open circuit voltage  |
| $J_{sc}$     | Short circuit current density   |
| FF           | Fill factor   |
| $P_{in}$     | Input power   |
| $P_{max}$    | Maximum power   |
| $I_{mp}$     | Current at maximum power point  |

|                |  |
|----------------|--|
| $V_{mp}$       | Voltage at maximum power point                             |
| $I_{sc}$       | Short circuit current                                      |
| $K_2CO_3$      | Potassium carbonate  |
| $Cs_2CO_3$     | Cesium carbonate   |
| $Na_2SO_4$     | Sodium sulphate  |
| KOH            | Potassium hydroxide  |
| $C_2H_5OH$     | Ethanol  |
| $CH_3OH$       | Methanol   |
| $Pd(OAc)_2$    | Palladium acetate  |
| $Pd(dppf)Cl_2$ | 1,1'-Bis(diphenylphosphino)ferrocene dichloropalladium(II) |
| $Pd(PPh_3)_4$  | Tetrakis(triphenylphosphine)palladium(0)                   |
| HCl            | Hydrochloric acid  |
| $(CH_2OH)_2$   | Ethylene glycol  |
| $(CH_3)_2O$    | Diethyl ether  |
| KBr            | Potassium bromide  |
| KI             | Potassium iodide   |
| $C_5H_5N$      | Pyridine   |
| $NaNO_2$       | Sodium nitrite   |