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RESEARCH INTERESTS

- **Synthesis and spectroscopic characterization of organic semiconductors for applications in optoelectronics and energy Storage Devices**
- **Molecular design and development of multifunctional conjugated polymers and oligomers with novel properties**

EDUCATION

Indian Institute of Science (IISc), Bangalore

PhD in Materials Science [July 2014 – June 2020]

Thesis Title: Studies on Quinoidal Diketopyrrolopyrrole Derivatives and their Applications

Indian Institute of Technology (IIT), Roorkee

MSc (Chemistry) [July 2012 – May 2014]

Cumulative Performance Index (CPI): **8.84/10**

BSc (Chemistry hons.) [July 2009 – May 2012]

Percentage of marks: **89.04***

St. Xavier's Senior Secondary school, Delhi

Grade 12th, CBSE Board [April 2009]

Percentage of marks: **96.0***

*: Aggregate of Science and Math Subjects

RESEARCH EXPERIENCE

Solid State and Structural Chemistry Unit (SSCU), Indian Institute of Science (IISc)

Project 1: Biradicaloid character in Quinoidal molecules

- Synthesized a series of donor-acceptor based quinoidal molecules to investigate the contribution and relative importance of the biradical form on the ground state electronic structure and distribution of spin density.
- The ground-state properties were systematically investigated by nuclear magnetic resonance (NMR) spectroscopy, single crystal X-ray diffraction and electrochemical studies.

Project 2: Molecular n-type doping of Organic Semiconductors

- N-doping of quinoidal DPP based small molecules has been systematically studied using air-stable molecular n-dopant N-DMBI in ambient atmosphere.
- In particular, transient spectroscopy and temperature dependent conductivity experiments revealed a drastic enhancement in photoconductivity of doped films and led to a better understanding of fundamental physics behind molecular doping of quinoidal derivatives.
- Thermally activated band transport observed at various doping concentrations reveals clear signatures of Fermi level pinning by donor (n-dopant) band and thereby suggests the charge transport mechanism as electron transfer from impurity band to the conduction band edge of organic semiconductor, rather than transport in band tails.

Project 3: Non-aqueous Redox Flow batteries

- Synthesized an air-stable π -conjugated Organic material for use as an anolyte.
- Demonstrated reversible CV voltammograms with different electrolytes at various scan rates.
- Comparative kinetic studies of diffusion coefficient for active material in each of the electrolyte systems.
- Tested different organic catholyte materials in combination with anolyte, building and testing a cell in static configuration.
- Future work: Construction of an all-organic redox flow battery using high- and low-potential active species.

PUBLICATIONS

1. **Sharma S.**; Ghosh S.; Ahmed T.; Ray S.; Islam S.; Salzner U.; Ghosh A.; Seki S.; Patil S. Fermi Level Pinning Induced by Doping in Air Stable N-type Organic Semiconductor. *ACS Applied Electronic Materials* **2020**, 2 (1), 66-73.
2. **Sharma S.**; Sakai N.; Ray S.; Senanayak S. P.; Sirringhaus H.; Snaith H. J.; Patil S. Inverted perovskite solar cells with air stable Diketopyrrolopyrrole-based electron transport layer. *Solar Energy* **2019**, 186, 9-16.
3. Ray S.; **Sharma S.**; Salzner S.; Patil S. Synthesis and Characterization of Quinoidal Diketopyrrolopyrrole Derivatives with Exceptionally High Electron Affinities. *J. Phys. Chem. C* **2017**, 121, 30, 16088-16097.
4. **Sharma S.**; Suman R.; Aetukuri N.; Shukla A. K.; Patil S. Diketopyrrolopyrrole Based Derivative for Non-Aqueous Redox Flow Battery. *ECS Meeting Abstracts* 2019, 3, 449-449.
5. **Sharma S.**; Suman R.; Aetukuri N.; Shukla A. K.; Patil S. Electrochemical Evaluation of Diketopyrrolopyrrole Derivatives for Non-aqueous Redox Flow Battery (Manuscript submitted).

PROJECTS

Singlet fission materials based on conjugated organic molecules

[Feb '17 – April '17]

Advisor: Prof. Sir Richard Friend, University of Cambridge

- Rationally designed and synthesized conjugated organic materials of significant relevance in organic photovoltaics and investigated the optical and electronic properties.
- Probed the photophysical dynamics using transient absorption to investigate the possibility of singlet exciton fission.

Novel Electron-transport material (ETM) for Inverted Perovskite Solar cells (PSCs)

[Sep '15 – Oct '15]

Advisor: Prof. Henry Snaith, University of Oxford

- Performed Fluorescence Quenching and Lifetime measurements between Perovskite layer coated and n-type organic semiconductor
- Fabricated devices with ETM in inverted planar heterojunction PSC employing $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ and $\text{FA}_{0.8}\text{Cs}_{0.2}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ as the active layer and PEDOT:PSS as the hole transporting material

INTERSHIPS

CSIR-Indian Institute of Chemical Technology, Hyderabad

[May '13 – July '13]

1. Project Title: Synthesis and Biological Evaluation of Diaryl Oxetane Derivative

Advisor: Dr. S. Chandrasekhar, Division of Natural Products Chemistry

Oxetane derivative possesses various biological activity like anti-cancer, cytotoxic, herbicidal, antibacterial, promotes growth of neurons, vasoconstriction, platelet aggregation, and bronchoconstriction. Apart from that oxetane ring has considerable effect on anticancer potency of Taxol and Docetaxol as well as insecticidal potency of EDO and Oxasulfuron. Hence, Diaryl oxetane skeleton was chosen for the present study and found to have biological activity.

School of Chemistry, University of Hyderabad

[May '11 – July '11]

Project Title: Synthesis of propargylamines, Allenes and Poly(N-methyl) Aniline

Advisor: Prof. M. Periasamy, University of Hyderabad

This project comprised of two parts 1) synthesis of propargylamines and allene, 2) synthesis of poly(N-methylaniline). The first part describes the synthesis of allene from zinc iodide mediated reaction of propargylamines. The second part deals with the synthesis of poly(N-methylaniline) by chemical polymerization of N-methylaniline.

Project Title: Testing of transformer oil

Advisor: *Dr. Subeer S. Majumdar, National Institute of Immunology, New Delhi*

DNA fragments were interpreted in mice genome by the technique known as electroporation, by injecting foreign gene into testes of mice.

TECHNICAL SKILLS

Programming Languages: C, C++

Scripting/Plotting Tools: OriginPro, ChemBioDraw, MestReNova, MS Excel, Origin

Characterization/Experimental Techniques: SEM, XRD, FT-IR, UV-Vis, GC-MS, Fluorometer, Fluorescence Lifetime Spectrofluorometer, Spin coater, Solar Simulator, Cyclic Voltammetry, Impedance spectroscopy

ACHIEVEMENTS

- Presented my research work via an oral talk on energy storage systems in **235th ECS Meeting** Symposium, Texas during 26th to 30th May 2019.
- Received “**Best presentation award**” in paper presentation held at IISc in 2016. The competition involved presenting research work and was judged on the basis of presentation skills and the quality of the research.
- Attended the Review cum discussion meeting: **UK-India Solar Energy Project**-Newton-Advancing the Efficiency and the Production potential of Excitonic Solar Cells (APEX)-II held at **Brunel University**, London in October 2015.
- Attended the APEX meeting held at IISER Pune in February 2016.
- Presented a brief review on Device development-Bulk heterojunctions at **DST-RCUK** consortium on the ‘Advancing the Efficiency and Production Potential of Excitonic Solar Cells (APEX)’ at **IIT Delhi** in February 2015.
- Qualified **GATE 2014** with an All India Rank of **153** amongst 7932 students.
- Qualified **IIT-JAM 2012** with an All India Rank of **186** amongst more than 15000 students. IIT-JAM is an entrance admission test jointly conducted by IITs for admission to MSc courses at reputed IITs.
- Awarded **DST-INSPIRE** scholarship for the academic year 2009-2014 (**awarded to only top 1% students based on their performance at the National level**)
- Awarded KPMG scholarship in 2011 awarded to students with a consistent and strong academic track record of excellence
- Stood **2nd rank** in **B.Sc. Chemistry (hons.) in Delhi University (DU)** for year 2012.
- Received “**Science Meritorious scholarship**” provided by **DU** in year 2010.
- Awarded “**Ramesh Goel Memorial Prize**” in year 2010-2011 for being the **best student** in II year at St. Stephen’s college, Delhi.
- Awarded “**Sardar Hansa Singh Memorial Chemistry Prize**” in year 2010-2011 at St. Stephen’s college, Delhi.
- Stood **1st rank** as school topper in Chemistry (98%) and Biology (95%) in the **AISSCE, 2009** at St. Xavier’s senior secondary school, Delhi.
- Awarded the “**Best Student Award**” by Dr. Sahib Singh Verma in year 2005.

RELEVANT COURSES

Core: Quantum Mechanics and Bonding, Symmetry and Group Theory, Thermodynamics and Surface Chemistry, Analytical Techniques, Modern Organic Chemistry, Advanced Coordination and Organometallic Chemistry, Kinetics and Photochemistry, Advanced Organic Structure, Conformations, Reactivity and Reactions, Asymmetric Synthesis, Molecular Spectroscopy, Advanced Organic Chemistry – I, Advanced Organic Chemistry – II, Organic Semiconductors : Synthesis and Applications

Electives: Crystal and Molecular Structure, Electroanalytical Chemistry, Group Dynamics

EXTRA – CURRICULAR ACTIVITIES

- Volunteered for INDO-German workshop on Renewable Energy (Organic Solar Cells) and Curriculum Innovation in Science Education held at SSCU, IISc Bangalore.
- Attended HORIBA Optical School held at JNCASR, Bangalore from 22nd May 2017 to 26th May 2017 jointly organized by JNCASR, Bangalore and HORIBA Scientific Group. The school was conducted to impart basic Optical Techniques and hands on training in Optical Instruments including Raman, Steady State Fluorescence and TCSPC Measurements System to potential researchers.
- Executive Council head of Chemistry Society, St. Stephen’s College, Delhi from the year 2010-12.

- Organized educational trip to National Institute of Immunology, NII, Delhi for all the students of Chemistry department at St. Stephen's College, Delhi.

REFERENCES

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Declaration

I, Dr. Shikha Sharma, hereby declare that the information given above is true to the best of my knowledge and belief and nothing has been hidden.



Dr. Shikha Sharma
PhD, Solid State and Structural Chemistry Unit (SSCU)
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Bangalore-560012

Fermi Level Pinning Induced by Doping in Air Stable n-Type Organic Semiconductor

Shikha Sharma,[†] Samrat Ghosh,[‡] Tanweer Ahmed,[§] Suman Ray,[†] Saurav Islam,[§] Ulrike Salzner,^{||} Arindam Ghosh,[§] Shu Seki,[‡] and Satish Patil^{*,†}

[†]Solid State and Structural Chemistry Unit and [§]Department of Physics, Indian Institute of Science, Bangalore-560012, India

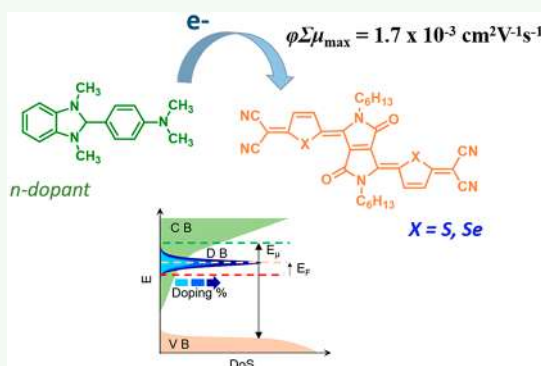
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^{||}Department of Chemistry, Bilkent University, 06800 Bilkent, Ankara, Turkey

Supporting Information

ABSTRACT: Doping of organic semiconductors enhances the performance of optoelectronic devices. Although p-type doping is well studied and successfully deployed in optoelectronic devices, air stable n-type doping was still elusive. We succeeded with n-type doping of organic semiconductors using molecular dopant N-DMBI under ambient conditions. Strikingly, n-type doping accounts for a gigantic increase of the photoconductivity of doped thin films. Electrical and optical properties of the n-doped molecular semiconductor were investigated by temperature dependent conductivity, electron paramagnetic resonance (EPR), and flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements. A significant reduction and saturation in activation energy with increasing doping level clearly suggests the formation of an impurity band and enhancement in carrier density. Computational studies reveal the formation of a charge transfer complex mediated by hydrogen abstraction as the rate-determining step for the doping mechanism. The colossal enhancement of photoconductivity induced by n-doping is a significant step toward optoelectronic devices made of molecular semiconductors.

KEYWORDS: molecular doping, organic semiconductor, photoconductivity, N-DMBI, Fermi level



1. INTRODUCTION

Molecular doping of organic semiconductors with electron acceptors (p-doping) or electron donors (n-doping) increases conductivities and enhances the performance of optoelectronic devices by lowering energy barriers for charge injection and reducing ohmic losses.^{1,2} Employment of doped multilayer structures has been successful in advancing the device efficiencies in organic photovoltaics,^{3–8} perovskite solar cells,⁹ and organic light emitting diodes (OLEDs).^{10–17} Especially, p-type doping is extensively studied for a wide range of different dopant/organic semiconductor combinations.^{18–21} In contrast, efficient n-type doping is more difficult to achieve, and a lack of stable n-type systems has so far limited the realization of p-i-n multilayer structures. To achieve n-type doping, semiconductor and dopant are required to fulfill the following conditions: (i) both the n-dopant and n-type semiconductor have to be stable in ambient atmosphere; and (ii) the electron affinity of semiconducting material should match or exceed the ionization potential of the dopant.^{22–24}

The first ever case of n-type molecular doping of organic semiconductors was achieved with tetrabutylammonium salts.²⁵ Recently, derivatives of reduced 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazoles (DMBI) such as

N-DMBI and DMBI dimers,^{26–29} e.g., (2-Cyc-DMBI)₂, have emerged as promising donors. Alternatively, radical ions produced by cleaving of organometallic complex dimers³⁰ such as Cr₂(hpp)₄ and (RuCp⁺(mes)₂)₂ can transfer electrons. Nevertheless, there have been few reports on synthesis and n-doping of small air stable molecular hosts at room temperature. Jen et al.³¹ reported n-doping of quinoindole nitrile (DCN) by ammonium and phosphonium salts in solution at room temperature, leading to conductivities around 10^{–2} S cm^{–1}. Bao et al.³² synthesized several n-dopant precursors based on benzimidazole derivatives for doping of fullerene in solution.

The practical utility of molecular doped organic semiconductors motivated extensive efforts to understand the fundamental doping mechanism,^{33–36} as microscopic understanding of the underlying physics and doping mechanism is still lacking. Recently, Ortmann and co-workers have used simulations and experimental techniques to resolve the Fermi

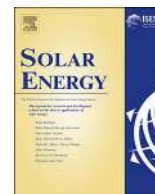
Special Issue: Young Investigator Forum

Received: November 6, 2019

Accepted: December 22, 2019

Published: January 6, 2020

Shikha S.



Inverted perovskite solar cells with air stable diketopyrrolopyrrole-based electron transport layer

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ARTICLE INFO

Keywords:

Diketopyrrolopyrrole
Perovskite solar cells

ABSTRACT

One of the possible causes of degradation of perovskite solar cells is the instability of the electron transporting layer. In this regard, design of air stable electron transport organic semiconductors, compatible with perovskite energy levels presents challenges due to inherent vulnerability to traps, presumably originating due to water and/or oxygen. In this work, we demonstrate air stability of diketopyrrolopyrrole-based molecule (TDPP-CN₄) at ambient conditions and its application as electron transporting layer (ETL) in perovskite solar cells. We investigated electron mobility and air stability of TDPP-CN₄ by fabricating top-gate bottom-contact (TG-BC) thin film transistors and compared with PCBM at ambient conditions. Both TDPP-CN₄ and PCBM exhibit electron transport properties with mobility of 0.13 cm² V⁻¹ s⁻¹ and 0.03 cm² V⁻¹ s⁻¹ respectively. However, we found remarkable air stability of the TDPP-CN₄ in the OFET measurements under ambient conditions. These excellent properties of TDPP-CN₄ render them as potential ETL layer in inverted planar heterojunction perovskite solar cells. Our preliminary device studies show remarkable short-circuit current (J_{sc}) ~ 17.4 mA/cm² with moderate open-circuit voltage (V_{oc}) of 0.50 V. These results suggest that the electron mobility and air-stability of diketopyrrolopyrrole-based molecule hold a promise as ETL in perovskite solar cells at ambient conditions.

1. Introduction

Among recently emerged photovoltaic concepts, organo-metal halide based perovskites have proved successful in terms of cost and efficiency but encountered materials and device instability from ambient humidity and oxygen in the air (Manshor et al., 2016). However, the simplicity and ease of device fabrication from solution with the realization of efficiencies > 21% made serious claims for commercialization as future photovoltaic technology (Yang et al., 2015). In a conventional perovskite solar cell, the device architecture constitutes the light-absorbing perovskite layer in a sandwiched configuration between mesoscopic metal oxide such as TiO₂, Al₂O₃, ZnO as electron transport layer (ETL) and organic semiconductors such as tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9-spirobifluorene (spiro-OMeTAD), poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) as hole transporting material (HTM) (Roldán-Carmona et al., 2015). Despite the high performance of such n-i-p structure based perovskite devices, the essential requirement of high temperature sintering process for the preparation of mesoporous TiO₂ layer and large photocurrent hysteresis pose an obstacle in determining accurate power conversion efficiencies and act

as a barrier to fabricate perovskite solar cells on flexible substrates (Gu et al., 2016). Contrary to this, the metal-oxide-free inverted device architecture (p-i-n) exploiting the planar heterojunction formed by halide perovskite with conventional organic transport layer poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) as HTM and fullerene derivative [6,6]phenyl-C₆₁-butyric acid methyl ester (PCBM) as ETL removes the restraint of extreme annealing temperatures (Docampo et al., 2013), which simplifies the cell configuration. At present, PCBM is the most commonly used ETL in inverted perovskite solar cells. The high electron affinity and reasonable charge carrier mobility makes PCBM suitable for promoting charge separation at the interface between perovskite and fullerene (Wu et al., 2015; Azimi et al., 2011). One of the major issues with PCBM is ambient instability, induced by hydrophilicity of ester group in the molecular backbone (Zhao et al., 2016). Furthermore, PCBM is also prone to photochemical transformation from monomer to dimeric/polymeric structures on exposure to light (Zhou et al., 1993). Relatively poor ambient and photostability as well as uninflected tunability (Zhao et al., 2016) of energy levels of PCBM layer are the major limitations towards improved device efficiency as well as further entangles the device fabrication process.

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<https://doi.org/10.1016/j.solener.2019.04.071>

Received 4 October 2018; Received in revised form 19 March 2019; Accepted 23 April 2019

Available online 06 May 2019

0038-092X/ © 2019 Published by Elsevier Ltd on behalf of International Solar Energy Society.

Synthesis and Characterization of Quinoidal Diketopyrrolopyrrole Derivatives with Exceptionally High Electron Affinities

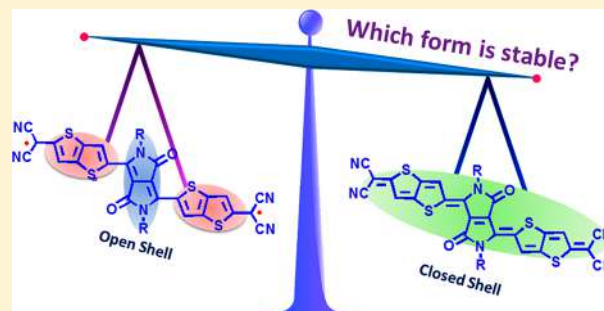
Suman Ray,[†] Shikha Sharma,[†] Ulrike Salzner,[‡] and Satish Patil^{*,†}

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S Supporting Information

ABSTRACT: Open-shell singlet biradicaloids are short-lived intermediates, but they exhibit fascinating properties for spin-based devices. Therefore, understanding the nature of their electronic structure and stability is critical for harnessing them in optoelectronic or spintronic devices. Toward this goal, we have synthesized a series of diketopyrrolopyrrole-based quinoidal molecules to investigate the contribution and relative importance of the biradical form on the ground-state electronic structure and distribution of spin density. Possibility of crossover from a closed-shell to an open-shell structure with increase in the C=C/C–C conjugation length was investigated. The ground-state properties were systematically investigated by nuclear magnetic resonance (NMR) spectroscopy, single-crystal X-ray diffraction, and electrochemical studies. Furthermore, *n*-doping has been carried out in solution at ambient conditions to understand the nature of doped species and demonstrate air stability. Doped species were probed by UV–visible and electron spin resonance (ESR) spectroscopy to unambiguously establish the generation of anionic species in solution. Experimental results are complemented by theoretical calculations to provide insight into the trend toward biradicaloid spin states with increasing conjugation length.



1. INTRODUCTION

π -Conjugated quinoidal molecules have emerged as promising materials because of their air stable *n*-channel electron transport in organic field-effect transistors,^{1–8} near-infrared (NIR) absorption,^{9–12} and nonlinear optical properties.^{12–14} Recent studies have also revealed the existence of open-shell biradical character for a series of donor–acceptor-based π -conjugated quinoidal molecules.^{13–18} Considering the inherent chemical reactivity of open-shell biradicals at ambient atmosphere, such properties are quite unusual.¹⁵ In these molecular systems, the contorted quinoidal forms with closed-shell singlet electronic ground states are strongly stabilized by π -electron delocalization along the oligoene-like inter-ring C=C/C–C alternating pattern.¹⁹ Contributions from closed-shell and open-shell forms through quinoid-aromatic resonance impart biradical character to these systems.¹³ In general, closed-shell singlet systems have electronic ground states with a large HOMO–LUMO gap. In quinoidal conjugated systems, small energy gaps allow mixing of the HOMO and LUMO, which results in biradical character of the ground states.¹⁵ The driving force for the emergence of an energetically stable open-shell biradical state is the regaining of the aromaticity of the quinoidal units because of their intrinsic preference for aromatic structures.^{19,20} A key point to consider is that the generation of biradical aromatic-like structures results in the dissociation of a π -bond of the corresponding quinoidal form, reducing π -conjugation. The energy required for the dissociation of the π -bond must be

compensated by the gained aromatic resonance energy in the generation of Kekule biradicals.²¹ Accretion of nonaromatic quinoidal units leads to further lowering of the band gap as well as additional aromatic resonance energy, which ultimately drives the crossover from the closed-shell (for short oligomeric chains) to the open-shell form (for extended systems).¹⁹ Hence, the biradical contribution to the ground-state electronic structure would be determined by the relative weight of aromatic and nonaromatic forms and increase with chain length.

Over the years, numerous open-shell singlet biradicaloids based on quinoidal π -conjugated molecules have been developed, including but not limited to quinoidal oligothiophenes,^{18,22–24} thienoacenes,^{8,11,12,20,25,26} and polycyclic hydrocarbons.^{16,17,21,27–38} These molecules with biradical character have many prospective applications in organic electronics,^{1–8,39–42} photonics,^{9–12,43} and spintronics devices.^{44–47}

The biradical character index (y_0) and singlet–triplet energy gap (ΔE_{S-T}) correlate with third-order nonlinear optical (NLO) responses and magnetic properties of open-shell singlet biradicals.^{19,48,49} However, extended π systems possessing large biradical character are generally unstable, which poses a profound challenge for the development of synthetic routes

Received: May 1, 2017

Revised: July 9, 2017

Published: July 10, 2017



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Diketopyrrolopyrrole Based Derivative for Non-Aqueous Redox Flow Battery

Shikha Sharma¹, Rathod Suman², Suman Ray¹, Nagaphani Aetukuri³, Ashok Kumar Shukla⁴ and Satish Patil²

Published 1 May 2019 • © 2019 ECS - The Electrochemical Society

ECS Meeting Abstracts, Volume MA2019-01, A03-Large Scale Energy Storage 10

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Shikha Sharma *et al* 2019 *Meet. Abstr.* **MA2019-01** 449

<https://doi.org/10.1149/MA2019-01/3/449>

Abstract

Non-aqueous Redox Flow Batteries (RFBs) exploiting the wider electrochemical potential gap between catholyte and anolyte operate at higher cell voltages and lead to high energy and power densities with compelling energy efficiencies. However, stable anolytes are rare, primarily due to their low stability in presence of oxygen and moisture. The inherent atmospheric reactivity of anolyte puts a formidable demand to judiciously design molecules with high electron affinity and electrochemical stability. In this study, a non-