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Stable and charge recombination minimized π -extended thioalkyl substituted tetrathiafulvalene dye-sensitized solar cells†

Lingamallu Giribabu,^{*a} Naresh Duvva,^a Surya Prakash Singh,^a Liyuan Han,^b Idriss M. Bedja,^c Ravindra Kumar Gupta^c and Ashrafal Islam^{*b}

Two new metal-free organic sensitizers have been designed based on tetrathiafulvalene scaffolds by implementing a donor- π -acceptor (D- π -A) approach in which thioalkyl substituted tetrathiafulvalene acts as a donor, substituted anthracene as a π -spacer and cyanoacrylic acid acts as an acceptor as well as an anchoring group. Spectroscopic, electrochemical and DFT studies confirmed the molecular integrity of both sensitizers. The onset of absorption of both sensitizers extends up to 600 nm in solution and up to 700 nm on nanocrystalline TiO₂. DFT studies specified that the HOMO is delocalized over the anthracene as well as the dithiole units, and the LUMO is delocalized over the anchoring group in both sensitizers. The new sensitizers have shown an improved efficiency of 7.15% in dye-sensitized solar cells using an I⁻/I₃⁻ redox couple. The enhanced efficiency might be due to the thioalkyl group wrapping over the anthracene π -spacer to prevent the recombination of electrons in the TiO₂ conduction band. Recombination studies indicate the regeneration of the oxidized dye due to the redox couple.

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Introduction

Dye-sensitized solar cells (DSSCs) have attracted interest for nearly two and half decades due to their low cost, easy fabrication and low environmental impact compared to conventional silicon photovoltaics.¹⁻⁶ The chemical nature and structure of a sensitizer play a crucial role in the development of high efficiency DSSCs. Since their first report in the 1990s, polypyridyl ruthenium(II) complexes have been the most commonly used sensitizers, leading to excellent photovoltaic performance, particularly with a high efficiency of over 11%.⁷⁻⁹ However, ruthenium(II) complexes are very expensive due to the rarity of the metal in the Earth's crust, intricate synthetic steps and purification methods, and are less durable due to the presence of -NCS groups in their molecular structure.¹⁰ Metal-free organic dyes, however, have attracted significant attention as promising alternatives by virtue of their large diversity in molecular structure, that can tune absorption

and HOMO-LUMO properties *etc.*, in a desired manner through suitable molecular design strategies.^{11,12} The most efficient organic sensitizers are composed of a donor (D) and an acceptor (A) linked through a π -bridge, whereby an effective intramolecular charge transfer can occur leading to the appearance of a broad and intense absorption band in the visible region. Among D- π -A sensitizers, a variety of organic donors including triphenylamine, phenothiazine, carbazole, porphyrin and indoline have been explored.¹³⁻¹⁶ To date, the best DSSC based on organic sensitizers showed an efficiency of *ca.* 10%.¹⁷

Because of the strong π -donor property of the tetrathiafulvalene scaffold, it has been widely used in materials chemistry and is predominantly used for optoelectronic applications.^{18,19} Essentially, TTF-based D- π -A systems have found numerous potential applications as their electrochemical and optical properties can be finely tuned by molecular engineering.^{20,21} In spite of this, only few examples were reported in the literature on extended π -conjugated tetrathiafulvalene (exTTF) based sensitizers for DSSCs.²²⁻²⁴ As the first example, exTTF-sensitized solar cells showed a moderate efficiency up to 3.8%.²² The low efficiency of these exTTF based sensitizers is probably due to the fact that they absorb only in the UV region and have an energetically high-lying HOMO, and therefore dye-regeneration after electron-injection is thermodynamically unfavourable. On the other hand, Liu and co-workers have designed a quinoxaline-fused tetrathiafulvalene based sensitizer with red-shifted absorption and show an overall conversion

^a Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Uppal Road, Tarnaka, Hyderabad 500607, India.

E-mail: giribabu@iict.res.in

^b Photovoltaic Materials Group, National Institute for Materials Science, Sengen 1-2-1, Tsukuba, Ibaraki 305-0047, Japan.

E-mail: Islam.Ashrafal@nims.go.jp

^c Cornea Research Chair, Optometry Department, College of Applied Medical Sciences, King Saudi University, Riyadh 11433, Saudi Arabia

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A Detailed Investigation into the Electrical Conductivity and Structural Properties of [Poly(ethylene oxide)-succinonitrile]-Li(CF₃SO₂)₂N Solid Polymer Electrolytes

Ravindra Kumar Gupta^{†,*} and Hee-Woo Rhee[‡]

[†]Cornea Research Chair, Department of Optometry, College of Applied Medical Sciences, King Saud University, Riyadh 11433, Saudi Arabia. *E-mail: rgupta@ksu.edu.sa

[‡]Department of Chemical and Biomolecular Engineering, Sogang University, Seoul 121-742, Korea
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A solid polymer electrolyte (SPE) was prepared via a solution casting method from a blend of equal weight fractions of poly(ethylene oxide) (PEO) and succinonitrile, used as the polymer matrix, and a salt, Li(CF₃SO₂)₂N ($x = 0-0.3$ in weight fraction). A plot of the electrical conductivity ($\sigma_{25^\circ\text{C}}$) vs. x showed an upturned U-shape, with the highest value being $\sim 3.9 \times 10^{-4}$ S/cm for $x = 0.25$ (EO/Li⁺ = 9.8; the optimum conducting composition). The electrolytes with x ranging from 0.15 to 0.3 showed a linear trend in their $\log(\sigma T^{0.5}) - (T - T_g)^{-1}$ curves with low pseudo-activation energy values, suggesting the presence of highly conductive amorphous domains, as confirmed by X-ray diffractometry measurements, Fourier-transform infrared (FT-IR) spectroscopy, polarized optical microscopy, and differential scanning calorimetry studies. The change in PEO chain conformation with x is discussed in detail using FT-IR spectroscopy in the light of earlier results reported for PEO – Li(CF₃SO₂)₂N SPEs.

Keywords: Polymer electrolyte, Poly(ethylene oxide), Succinonitrile, Electrical conductivity
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Introduction

Lithium-ion conducting solid polymer electrolytes (SPEs) are highly attractive materials for solid-state electrochemical devices because of their compactness, ruggedness, chemical and mechanical stability, and safety.¹⁻⁷ Poly(ethylene oxide), commonly abbreviated as PEO, is used in the preparation of SPEs for the investigation of all-solid-state batteries. PEO is thermally stable up to 200°C, environmentally friendly, and non-toxic; moreover, it is inexpensive. PEO solvates salts owing to its high dielectric constant (ϵ , 5–8) and, at temperatures greater than the glass transition temperature (T_g), aids ion transport via interactions between the ions and the ethereal oxygen of the polymeric chains.⁶ PEO–LiX electrolytes, where X is an anion, show poor electrical conductivity ($\sigma_{25^\circ\text{C}} < 10^{-5}$ S/cm) at the optimum conducting composition (OCC). This is because of the very high crystallinity of PEO, which results from the highly crystalline PEO domains containing long and linear polymeric chains at the OCC. In other words, only a few highly conductive amorphous domains form at the OCC on salt solvation/complexation. In addition, the amorphous domains are also poorly interconnected, resulting in relatively low ionic mobility.

The crystallinity of PEO has been reduced in PEO-based SPEs by modifying the polymer chains via grafted polymers, block copolymers, and cross-linked polymer networks.¹⁻⁹ These modifications increase the size and

interconnectivity of the amorphous domains, resulting in $\sigma_{25^\circ\text{C}}$ values of $\sim 10^{-4}$ S/cm.

A simple and cost-effective methodology, the blending of two polymers, has also been used to reduce the crystallinity of PEO. For example, PEO has been blended with polymers such as poly(vinylidene fluoride)¹⁰ and polydimethylsiloxane.¹¹ However, these blends have $\sigma_{25^\circ\text{C}}$ values less than 10^{-4} S/cm. Succinonitrile (SN), a low-molecular-weight plastic crystal, has also been used as a blender to reduce the crystallinity of PEO.¹²⁻²⁴ For PEO – SN – LiX SPEs, SN acts as a plasticizer. These SPEs exhibit $\sigma_{25^\circ\text{C}}$ values ranging from 10^{-5} to 10^{-3} S/cm, where X indicates Cl, BF₄, PF₆, ClO₄, CF₃SO₃, (CF₃SO₂)₂N, (C₂F₅SO₂)₂N, B(C₂O₄)₂, or C₆F₃N₄.¹²⁻²⁴ The SN acted as a solid solvent because of its low melting temperature ($T_m \sim 54^\circ\text{C}$) and high ϵ (~ 55), which enables the dissolution of various types of salts with a better shape situation.²⁵⁻²⁷ SN also offers high molecular diffusivity between the crystal to plastic crystal phase transition temperature (T_{pc} , -35°C) and melting temperature,²⁵⁻²⁷ which is mediated by the trans-gauche isomerization (involving rotation about the central C–C bond) of the molecules and molecular jumps from one diagonal position of the body-centered cubic structure to another. The plastic phase has a high concentration of “trans” isomers as an impurity, and these are responsible for the high ionic conductivity.¹²⁻²⁴

A nearly equal weight fraction of PEO and SN results in PEO–SN blend with electrical conductivity better than that



Cyclometalated ruthenium complexes with 6-(*ortho*-methoxyphenyl)-2,2'-bipyridine as panchromatic dyes for dye-sensitized solar cells

Ryuji Kaneko ^a, Guohua Wu ^a, Kosuke Sugawa ^a, Joe Otsuki ^{a,*}, Ashraful Islam ^{b,**}, Liyuan Han ^b, Idriss Bedja ^c, Ravindra Kumar Gupta ^c

^a College of Science and Technology, Nihon University, 1-8-14 Kanda Surugadai, Chiyoda-ku, Tokyo 101-8308, Japan

^b National Institute for Materials Science (NIMS), Photovoltaic Materials Group, Sengen 1-2-1, Tsukuba 305-0047, Japan

^c Cornea Research Chair, Department of Optometry, College of Applied Medical Sciences, King Saud University, Riyadh 11433, Saudi Arabia

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ABSTRACT

A cyclometalated ruthenium complex with 6-(*ortho*-methoxyphenyl)-2,2'-bipyridine (MeO-L) and tricarboxyterpyridine ($\text{tpy}(\text{CO}_2\text{H})_3$) (**RuCC-PF₆**) was prepared, characterized, and evaluated as a dye for dye-sensitized solar cells (DSSCs). The first oxidation and reduction potentials are +0.99 V and -0.81 V vs NHE, respectively. This complex exhibits panchromatic absorption spectrum extending up to 800 nm. The transitions upon visible light excitation were mixtures of metal-to-ligand ($\text{Ru} \rightarrow \text{tpy}(\text{CO}_2\text{H})_3$) and interligand ($\text{MeO-L} \rightarrow \text{tpy}(\text{CO}_2\text{H})_3$) charge transfer transitions. Adsorption of the ruthenium complex on TiO_2 was carried out from solutions of **RuCC-PF₆** in the free acid form or solutions of **RuCC-(NBu₄)₂** in a deprotonated carboxylate form. The DSSC devices employing these complexes as the dye sensitizers generate electricity in response to light over the whole visible range and into the near infrared region over 900 nm. Remarkably, **RuCC-(NBu₄)₂** recorded higher short-circuit current density than a benchmark N719, while the open-circuit voltage was lower, resulting in a modest overall photon-to-current conversion efficiency of 6.4%. The transient absorption and electrochemical impedance spectroscopy have been conducted to get insight into the mechanistic details of the DSSC cells, which suggested that the presence of NBu₄ cation was beneficial in retarding the unwanted recombination reaction. Considering the efficient charge injection and regeneration as manifested by the large short-circuit current, modification based on the present structure would be a promising strategy toward higher efficiency dyes for DSSCs.

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1. Introduction

Developing better solar cells is an important issue for wider harvesting of solar energies [1]. Dye-sensitized solar cells (DSSCs) are one of the strong candidates for next-generation solar cells [2–4]. Although DSSCs with organic dyes have made efficiency records recently [5,6], ruthenium polypyridyl complexes still occupy the special position due to the accumulated studies and high efficiencies. The benchmark ruthenium dyes, N719 [7] and Black Dyes [8], however, are not without weakness. The thiocyanate ligand used in these dyes is monodentate and thus prone to

dissociation under operating conditions, thus leading to degradation in long-term use [6,9]. To overcome this problem, cyclometalated [10,11] and other multidentate ruthenium complexes [12,13] have attracted attention. Multidentate ligands are potentially more inert to dissociation and, as a bonus, the chemically modifiable to tune the properties, which is impossible for the thiocyanate ligand.

With applications to DSSCs in mind, we have previously studied the heteroleptic ruthenium complexes carrying 6-(*ortho*-methoxyphenyl)-2,2'-bipyridine (MeO-L) as one of the ligands and 4'-(4-tolyl)-2,2';6',2''-terpyridine as the other [14]. We obtained two types of complexes with MeO-L, one in which a carbon coordinates to the metal and the other in which the oxygen coordinates to the metal. We speculated that former complex would be promising for application to DSSCs on the basis of its HOMO and LUMO levels. In the present study, we have prepared a new ruthenium complex (**RuCC-PF₆**, Chart 1) with MeO-L and 2,2':6',2''-terpyridine-4,4',4''-

* Corresponding author.

** Corresponding author.

E-mail addresses: otsuki.joe@nihon-u.ac.jp (J. Otsuki), ISLAM.Ashraful@nims.go.jp (A. Islam).

Donor- π -Acceptor Based Stable Porphyrin Sensitizers for Dye-Sensitized Solar Cells: Effect of π -Conjugated Spacers

Narra Vamsi Krishna,^{†,‡} Jonnadula Venkata Suman Krishna,^{†,‡} Surya Prakash Singh,^{†,‡} Lingamallu Giribabu,^{*,†,‡,§} Liyuan Han,[§] Idriss Bedja,^{||} Ravindra Kumar Gupta,^{||} and Ashraful Islam^{*,§}

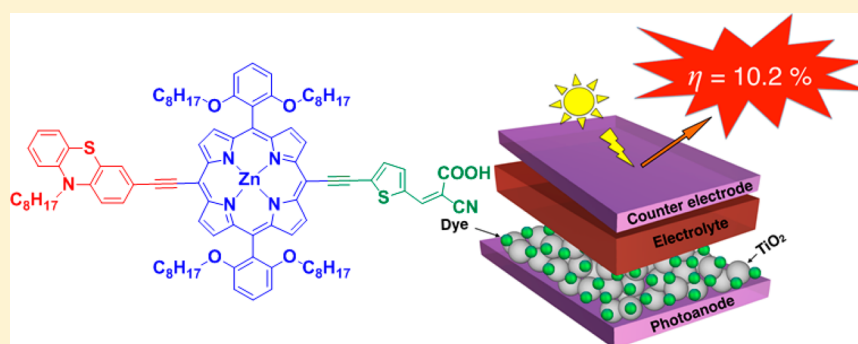
[†]Inorganic & Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Tarnaka, Hyderabad 500007, India

[‡]Academy of Scientific and Innovative Research, New Delhi, India

[§]Photovoltaic Materials Unit, National Institute for Materials Science, Sengen 1-2-1, Tsukuba, Ibaraki 305-0047, Japan

^{||}Cornea Research Chair, Department of Optometry, College of Applied Medical Sciences, King Saud University, Riyadh 11433, Saudi Arabia

S Supporting Information



ABSTRACT: Porphyrins are major sensitizers in dye-sensitized solar cells (DSSCs) and result in very high power conversion efficiency; however, aggregation tendency and visible range absorption prevent realistic applications. Thus, designing of novel porphyrins based sensitizers is essential to resolve the current existing issues. In this context, seven D- π -A porphyrin dyes (LG1–LG7) engineered with 3-ethynyl phenothiazine tethered at the meso-position and π -spacers, such as 4-ethynyl phenyl (LG1), 5-ethynylthiophene (LG2), 5-ethynyl furan (LG3), 2,1,3-benzothiadiazole (BTD)–phenyl (LG6), and BTD–thiophene (LG7), were incorporated between porphyrin macrocycle and anchoring carboxylic acid. Similarly, π -spacers 4-ethynyl phenyl (LG4) and 4-ethynylthiophene (LG5) were functionalized between porphyrin and anchoring cyanoacrylic acid. LG5 and LG6 showed significant near-infrared absorption resulting in the highest efficiency of 10.20% and 9.64% among other derivatives. UV–vis–NIR absorption, cyclic voltammetry, and density functional theory calculations of LG1–LG7 suggested that LG5 exhibits strong absorption, and optimized lowest unoccupied molecular orbitals aid to inject electrons very effectively from the excited state of dye into the TiO₂ conduction band. Current density–voltage (J – V) of LG1–LG7 revealed that LG5 exhibits the highest short-circuit current density of 21.01 mA cm⁻², resulting in a power conversion efficiency of 10.20% in a liquid I⁻/I₃⁻ redox couple electrolyte. Panchromatic incident photon-to-current conversion efficiency response of LG5 was observed between 400 and 900 nm, when compared to other derivatives. Thus, these results suggest that LG5 attained the highest efficiency in liquid electrolyte based DSSCs. Subsequently, durability studies of LG5 performed by continuous light exposure have shown that this sensitizer retained 80% initial efficiency after 1000 h. Therefore, the effect of spacer length and anchoring significantly contributed to improve the efficiency in liquid electrolyte, which is very useful to make efficient future generated DSSCs.

1. INTRODUCTION

With the potential of becoming a clean and renewable energy source, dye-sensitized solar cells (DSSCs) have drawn much attention because of their relatively high photovoltaic efficiencies, lower production cost, and aesthetic features of vivid color and transparency.^{1–8} Even though DSSCs have crossed a certified efficiency of >11%, almost all components of the device have to be redesigned to enhance the durability and lead to the effectiveness of the device cost. The sensitizer is one of the indispensable components of the device, and extensively used

sensitizers are Ru(II) polypyridyl complexes.^{9–13} Irrespective of their high conversion efficiency, the main drawbacks of Ru(II) polypyridyl complexes are their expense due to the rarity of the metal in the Earth's crust, and the lack of absorption in the near-IR region of the visible spectrum, where the solar flux of photons is still significant, thus limiting the realization and usability of

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Effect of spacers and anchoring groups of extended π -conjugated tetrathiafulvalene based sensitizers on the performance of dye sensitized solar cells†

Lingamallu Giribabu,^{*a} Naresh Duvva,^a Seelam Prasanthkumar,^a Surya Prakash Singh,^a Liyuan Han,^b Idriss Bedja,^c Ravindra Kumar Gupta^c and Ashrafal Islam^{*b}

Four new extended π -conjugated tetrathiafulvalene (ex-TTF) based dyes featuring a donor– π –acceptor (D– π –A) configuration with varying π -spacers and anchoring groups were synthesized and characterized. The sensitizer having the 4-ethynyl phenyl π -spacer (G4) shows red shifted absorption maxima in comparison with the sensitizer having only the phenyl π -spacer (G2). All four sensitizers undergo reversible oxidations to form stable radical cations. TDDFT calculations highlighted that the LUMO of the G4 sensitizer is more stabilized by the incorporation of the ethynyl group between the π -spacer and the cyanoacrylic acid anchoring group that aid to inject electrons efficiently into TiO₂ thereby resulting in an enhanced power conversion efficiency of 6.36% when compared to the other derivatives, which is also confirmed by the intensity-modulated photovoltage spectroscopy (IMVS) method. Kinetic studies demonstrated that fast regeneration of the oxidized dye by the redox couple is an important factor behind enhanced efficiencies in solar cells. Finally, the performance of the present sensitizers is compared to that of previously reported sensitizers.

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Introduction

Dye-Sensitized Solar Cells (DSSCs) have attracted interest for over two and half decades because of their ease of fabrication, flexibility and low environmental impact compared to conventional solid-state p–n junction photovoltaic devices.^{1–8} The sensitizer is one of the vital components in achieving high efficiency and durability of the device. Among various classes of sensitizers, Ru(II) polypyridyl complexes are widely used in view of their broad absorption through the metal-to-ligand charge transfer (MLCT) transition and their long excited state lifetimes.^{9–11} However, the rarity of Ru metal in the Earth's crust and cost due to intricate synthesis and purification steps might impede commercialization of the technology. Recently, a new class of compounds *i.e.*, metal-free organic dyes have been found to be alternatives based on the tunability of their optical and electrochemical properties in a desired manner through suitable molecular design strategies.^{12–15} Organic dyes showing good efficiencies are composed of a donor (D) and an acceptor

(A) linked through a π -bridge and one can efficiently tune their optical properties.^{16–18} By adopting the D– π –A approach, great varieties of metal-free organic dyes have been reported with a record efficiency of 14%.¹⁹

Tetrathiafulvalene (TTF) scaffolds have a wide range of applications in materials chemistry towards molecular optoelectronics.^{20,21} A few TTF scaffold based sensitizers have been reported in the literature.^{22–24} Grätzel and co-workers reported extended π -conjugated tetrathiafulvalene (ex-TTF) based sensitizers for DSSCs with an efficiency of 3.8%.²⁴ The low efficiency of ex-TTF sensitizers is due to their energetically unfavourable HOMO level, in which dye-regeneration after electron-injection is thermodynamically not feasible. Geng *et al.* studied the effect of π -linkers between the donor tetrathiafulvalene scaffold and anchoring groups on optical and electronic properties, achieving an overall device conversion efficiency of 0.87%.²² Recently, our group have reported ex-TTF based sensitizers by introducing long alkyl chains and changing the π -linker, achieving an overall conversion efficiency of 7.15%.²⁵ Motivated by these results, we have designed four new D– π –A sensitizers constituted with ex-TTF as the donor and either cyanoacrylic acid or rhodanine acetic acid as the acceptor. The change of π -linkers between the donor and acceptor units of dyes might tailor their frontier orbital energy levels to be beneficial to red shift the charge-transfer transition. In the present manuscript, we report the synthesis, characterization, optical and electrochemical properties, and recombination/dye regeneration kinetic study of four dyes as well as their application in DSSCs.

^aInorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Uppal Road, Tarnaka, Hyderabad 500607, India. E-mail: giribabu@iict.res.in

^bPhotovoltaic Materials Group, National Institute for Materials Science, Sengen 1-2-1, Tsukuba, Ibaraki 305-0047, Japan. E-mail: Islam.Ashrafal@nims.go.jp

^cCornea Research Chair, Optometry Department, College of Applied Medical Sciences, King Saudi University, Riyadh 11433, Saudi Arabia

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Effect of different auxiliary ligands and anchoring ligands on neutral thiocyanate-free ruthenium(II) dyes bearing tetrazole chromophores for dye-sensitized solar cells



Guohua Wu^a, Ryuji Kaneko^a, Kosuke Sugawa^a, Ashraf Islam^{b, **}, Idriss Bedja^c, Ravindra Kumar Gupta^c, Liyuan Han^b, Joe Otsuki^{a, *}

^a College of Science and Technology, Nihon University, 1-8-14 Kanda Surugadai, Chiyoda-ku, Tokyo 101-8308, Japan

^b National Institute for Materials Science (NIMS), Photovoltaic Materials Group, Sengen 1-2-1, Tsukuba 305-0047, Japan

^c Department of Optometry, College of Applied Medical Sciences, King Saud University, Riyadh 11433, Saudi Arabia

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ABSTRACT

Four new bistridentate Ru(II) complexes having a combination of ligands, 4,4'-dicarboxy-2,2':6,2''-terpyridine or its 2-hexylthiophene-substituted derivative as the anchoring ligand on one hand and one of tetrazolylpyridine-based ligands having a N⁺N⁺ coordination pattern or C⁻N⁺ coordination pattern as the auxiliary ligand on the other are reported as sensitizers for dye-sensitized solar cells (DSSCs), along with their spectroscopic, electrochemical, and theoretical characterizations. For the anchoring ligand, the introduction of 2-hexylthiophene unit leads to narrower spectral response and lower molar extinction coefficients and a smaller driving force for dye regeneration. For the ancillary ligand, the cyclometalating Ru–C bond induces a red shift in absorption compared with a Ru–N bond and thus affords a photocurrent generation at wavelengths of up to 950 nm. Further, the overall efficiencies of DSSCs are higher with the N⁺N⁺ complexes than with the C⁻N⁺ complexes, mainly due to higher open-circuit voltages (V_{oc}). Overall, the DSSC based on the bistetrazolate dye without the hexylthiophene unit for the anchoring ligand and having the N⁺N⁺ coordination pattern for the auxiliary ligand exhibited the highest efficiency of 5.9% when employing 0.5 M *t*-butylpyridine in the electrolyte.

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1. Introduction

Since dye-sensitized solar cells (DSSCs) based on modified nanocrystalline TiO₂ surfaces first appeared in a quarter century ago [1], bidentate 4,4'-dicarboxy-2,2'-bipyridine and tridentate 4,4',4''-tricarboxy-2,2':6,2''-terpyridine were extensively employed as the typical anchoring ligand in thiocyanate (NCS) based [2–10] and NCS-free [11–18] ruthenium complexes. In comparison with Ru(II) dyes with the bidentate structure, those with the tridentate structure exhibited superior absorption response in the near IR region.

It has been recently demonstrated that only two carboxy groups each substituted on a pyridine ring in the terpyridine-based anchoring ligand are sufficient for stable adsorption of the complex on TiO₂ surface [19]. For the dicarboxyterpyridine anchor, the two carboxy groups can be substituted on the terminal pyridine rings [20] leaving the central pyridine ring open or one on the terminal and the other on the central pyridine ring leaving a terminal ligand open [5,21–23]. In these two molecular designs, the remaining pyridine group without the carboxy group becomes available for further functionalization. The Ru(II) complexes with the former anchoring ligand substituted with dicarboxy groups on the terminal pyridine rings showed higher fill factor values but achieved only moderate efficiencies even if functional units were introduced on the middle pyridine ring to provide electron donating abilities and expand the π -conjugation system [20]. In the latter molecular design, functional units have been attached to the 3, 4, 5, and 6-positions of the terminal pyridine unit of 4,4'-dicarboxy-2,2':6,2''-terpyridine, such as

* Corresponding author.

** Corresponding author.

E-mail addresses: wllwgh1988@gmail.com (G. Wu), csry15015@nihon-u.ac.jp (R. Kaneko), sugawa.kosuke@nihon-u.ac.jp (K. Sugawa), ISLAM.Ashraf@nims.go.jp (A. Islam), bedja@ksu.edu.sa (I. Bedja), rgupta@ksu.edu.sa (R.K. Gupta), han.liyuan@nims.go.jp (L. Han), otsuki.joe@nihon-u.ac.jp (J. Otsuki).



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Heteroleptic Ru(II) cyclometalated complexes derived from benzimidazole-phenyl carbene ligands for dye-sensitized solar cells: an experimental and theoretical approach†

Tejaswi Jella,^{ab} Malladi Srikanth,^c Yarasi Soujanya,^c Surya Prakash Singh,^{ab} Lingamallu Giribabu,^{*ab} Ashrafal Islam,^{*d} Liyuan Han,^d Idriss Bedja^e and Ravindra Kumar Gupta^e

We have designed and synthesized two new ligands based on N-heteroleptic/phenyl carbene (NH-phenyl C) *i.e.*, 1-benzyl-2-(3,5-bis(trifluoromethyl)phenyl)-1H-benzod[*d*]imidazole (**L1**) and 3-(1-benzyl-1H-benzol-2-yl)-10-hexyl-10-*H*-phenothiazene (**L2**), used as ancillary ligands to heteroleptic Ru(II) complexes for dye-sensitized solar cells. Both NCS groups of the **N719** sensitizer are replaced with **L1** (**TC-1**) and **L2** (**TC-3**) to obtain cyclometalated Ru(II) complexes and one of 4,4'-dicarboxylato-2,2'-bipyridine (dcbpy) with **L1** to obtain a heteroleptic Ru(II) complex (**TC-2**). The presence of two trifluoromethyl groups of the **L1** ligand stabilizes the HOMO level of Ru(II) complexes and the presence of a phenothiazine moiety of the **L2** ligand alters the absorption properties of the **TC-3** complex. Both the ligands and the heteroleptic Ru(II) complexes are characterized by elemental analyses, ESI-MS, ¹H NMR, absorption and emission spectroscopy as well as electrochemical methods. The absorption spectra of **TC-1** and **TC-3** are blue shifted, when compared to the standard **N719** sensitizer. The assessment of these newly designed cyclometalated and heteroleptic Ru(II) complexes has revealed that **TC-2** exhibits an efficiency of 7.63%, whereas **TC-1** has an efficiency of 6.39% using an I⁻/I₃⁻ redox couple. DFT and nanosecond transient absorption kinetic studies have been adopted to understand the low efficiency of the **TC-3** complex.

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Introduction

Dye-sensitized solar cells (DSSCs) are being investigated extensively for their use in renewable energy technologies because of their great potential in terms of low fabrication cost, and flexible and high light-to-electrical energy conversion efficiency.^{1–8} DSSCs have achieved power conversion efficiencies of over 11%, which was demonstrated using a prototype device with

bis(tetrabutylammonium)-*cis*-di(thiocyanato)-*N,N'*-bis(4-carboxylato-4'-carboxylic acid-2,2'-bipyridine)ruthenium(II) (the **N719** dye) and trithiocyanato-4,4'-tricarboxy-2,2':6',2''-terpyridine ruthenium(II) (the black dye) sensitizers.^{9–12} In spite of this, these sensitizers show insufficient light-harvesting efficiencies in the near-IR region of the absorption spectra. The sensitizers are one of the key components in DSSCs as they absorb sunlight and induce intramolecular charge transfer from the ancillary ligand to the anchoring ligand with consequent electron injection into the conduction band of the TiO₂ semiconductor. For this reason, numerous heteroleptic ruthenium complexes have been probed, where one of the two 4,4'-dicarboxylato-2,2'-bipyridine (dcbpy) anchoring ligands has been replaced by a functionalized 2,2'-bipyridine (bpy) ligand with either hydrophobic chains to improve the device stability or with extended π -conjugated systems that include thiophene, carbazole, triphenylamine, coumarine *etc.*, to enhance the optical properties.^{13–22} Despite their stability and efficiency, modification of *N,N* ancillary ligands involves tedious synthetic protocols that will affect the cost of the sensitizer. In contrast, Grätzel and co-workers reported cyclometalated ruthenium polypyridyl complexes by replacing the NCS ligand with an anionic carbon atom, C⁻N as an alternative

^a Inorganic & Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, and CSIR-Network Institutes for Solar Energy (CSIR-NISE), Tarnaka, and CSIR-Network Institutes for Solar Energy (CSIR-NISE), Hyderabad-500007, Telangana, India. E-mail: giribabu@iict.res.in; Fax: +91-40-27160921; Tel: +91-40-27191724

^b Academy of Scientific and Innovative Research (AcSIR), New Delhi, India

^c Molecular Modelling Group, CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, Telangana, India

^d Photovoltaic Materials Unit, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

^e CRC, Optometry Department, College of Applied Medical Sciences, King Saudi University, Riyadh 11433, Saudi Arabia

† Electronic supplementary information (ESI) available: ESI-MS, ¹H NMR spectral data of all compounds and tables of molecular orbital composition and calculated absorption spectral wavelength data. See DOI: 10.1039/c6qm00264a

Cationic effect on dye-sensitized solar cell properties using electrochemical impedance and transient absorption spectroscopy techniques

Ravindra Kumar Gupta and Idriss Bedja

Cornea Research Chair, Department of Optometry, College of Applied Medical Sciences, King Saud University, PO Box 10219, Riyadh 11433, Saudi Arabia

E-mail: rgupta@ksu.edu.sa and bedja@ksu.edu.sa

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Abstract

Redox-couple polymer electrolytes, (poly(ethylene oxide)-succinonitrile) blend/MI-I₂, where M = Li or K, were prepared by the solution cast method. Owing to the plasticizing property of K⁺ ions, the K⁺ ion-based electrolyte exhibited better electrical conductivity than the Li⁺ ion-based electrolyte, which did however exhibit better photovoltaic properties.

Electrochemical impedance spectroscopy revealed faster redox species diffusions and interfacial processes in the Li⁺ ion-based dye-sensitized solar cells than in the K⁺ ion-based ones. Transient absorption spectroscopy ascertained faster dye-regeneration by the Li⁺ ion-based electrolyte than the K⁺ ion-based electrolyte.

Keywords: dye-sensitized solar cell, cationic effect, electrochemical impedance spectroscopy, transient absorption spectroscopy

 Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

The research on photovoltaic (PV) cells is currently gaining impetus worldwide due to global warming and pollution problems, energy crises and the abundant availability of sunlight. The area of dye-sensitized solar cells (DSSCs) is becoming more attractive because of their simple cell structure and cost-effectiveness regarding materials and manufacturing [1, 2]. A conventional DSSC—also known as a Gratzel cell—has the following structure: current collector (CC)/dye-sensitized nanostructured mesoporous semiconducting layer/redox mediator/counter electrode (CE, which is usually a platinum layer)/CC [1, 2]. The CC is a fluorine-doped tin oxide (FTO) conducting and transparent layer on a glass plate. The semiconductor is an n-type material, e.g. TiO₂. Because of the n-type nature of the semiconductor, the conventional cell is also known as n-type DSSC. The photon of the sunlight is

absorbed by a thin layer of dye molecule on the mesoporous TiO₂. The redox mediator is, in general, an I⁻/I₃⁻-based redox-couple liquid electrolyte that exhibits a maximum photon-to-current conversion efficiency (η) of 11.3% [3]. Recently, a Co^{3+/2+}-based redox-couple liquid electrolyte showed a record efficiency of 13% [4]. As shown in figure 1, the n-type DSSC works through the reactions, R0–R7 [1, 2, 5, 6]. The absorption of a photon by a dye molecule (*S*) results in a dye molecule (*S*^{*}) with an excited state (R0), followed by its oxidation (*S*⁺) and the injection of an electron (*e*⁻) to the conduction band (CB) of the TiO₂ (R2). The *S*⁺ at the excited state returns immediately back to the ground state by a process, R1. The generated electron (*e*_{CB}) migrates through mesoporous TiO₂ (R4) to CC and then a load, and finally reaches CE through FTO glass. At the CE/electrolyte interface, the electron reduces I₃⁻ and regenerates I⁻ (R7). The dye regeneration (ground state *S*⁺ to *S*) takes place via oxidation of I⁻,



Electrical, structural, and thermal properties of succinonitrile-LiI-I₂ redox-mediator



Ravindra Kumar Gupta^{a,*}, Idriss Bedja^a, Ashraful Islam^b, Hamid Shaikh^c

^a Cornea Research Chair, Department of Optometry, College of Applied Medical Sciences, King Saud University, P.O. Box 10219, Riyadh 11433, Saudi Arabia

^b National Institute for Materials Science (NIMS), Photovoltaic Materials Group, Sengen 1-2-1, Tsukuba 305-0047, Japan

^c SABIC Polymer Research Center, Department of Chemical Engineering, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

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ABSTRACT

We synthesized a solid I^-/I_3^- -based redox-couple electrolyte using a mixture of succinonitrile, LiI and I₂. An increase of LiI to succinonitrile mole ratio (x) up to 2.5% led to a fast rise in the electrical conductivity ($\sigma_{25^\circ\text{C}}$) of the electrolytes. Further increase in x slowly increased the $\sigma_{25^\circ\text{C}}$ -value. The composition with $x = 5\%$ achieved the highest $\sigma_{25^\circ\text{C}}$ -value ($\sim 1.6 \times 10^{-3} \text{ S cm}^{-1}$) and was referred to as the optimum conducting composition (OCC) of the electrolytes. Also, an increase of x led to a decrease of the melting temperature of the electrolytes as suggested by the $\log \sigma - T^{-1}$ study and ascertained by the differential scanning calorimetry study. The $\log \sigma - T^{-1}$ study showed a linear trend before and after the melting temperature, and the activation energy increased with increasing x -value. The electrical and thermal properties were explained using the vibrational spectroscopy study. The ionic transference number measurement showed that the electrolytes with $x = 4$ and 5% are predominantly ionic in nature.

1. Introduction

Renewable energy sources are currently highly demanding because of the environmental issues. The high rise of levels of greenhouse gases and pollution especially in developed and developing countries is leading to a potential mass destruction of the humankind through negative environmental effects. One of the renewable energy sources, the solar cell, is highly useful in a country like Saudi Arabia, where solar irradiance is quite high [1]. The dye-sensitized solar cell (DSSC), a third-generation solar cell, offers simple cell structure and cost-effectiveness in materials and manufacturing as compared to other solar cells [2]. Short energy payback time (< 1 year), enhanced performance under real outdoor conditions and capturing of light from all angles of the incident are some of the interesting features of the DSSCs. In the conventional DSSC, an I^-/I_3^- -based redox-couple liquid electrolyte is used for dye regeneration at the working electrode (WE; mesoporous TiO₂ layer) [2,3]. The dye regeneration occurs via oxidation of I^- producing I_3^- . The reduction of I_3^- into I^- occurs at the counter electrode (platinum layer). A fast diffusion of redox-couple is required for the efficient cell operation [3]. At present, the highest cell efficiency, $\eta \sim 11.1\%$, is reported for the liquid electrolyte: 0.6 M dimethyl propyl imidazolium iodide, 0.1 M LiI, 0.05 M iodine, and 0.5 M tert-butylpyridine (TBP) in acetonitrile [4]. The mixture, LiI-I₂ produces $I^-/$

I_3^- -redox-couple in the solution. The additive, TBP generally helps to increase the open circuit voltage of the cell by shifting the WE's conduction band towards higher energy. A use of imidazolium ionic liquid helps to increase the electrical conductivity and decrease the evaporation rate of the acetonitrile. A use of liquid electrolyte makes the cell prone to leakage of solvent especially at elevated operating temperature conditions due to the internal pressure. It also creates scale-up problem of manufacturing. The cell requires hermetic sealing too. Therefore, a solid electrolyte is required to meet the harsh environmental conditions as observed in gulf countries. For a review, see references, [2,3,5].

Succinonitrile (SN; $\text{N}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{N}$) is a non-ionic and low-molecular-weight plastic crystal, which has a plastic crystal phase between -38°C (crystal to plastic crystal phase transition temperature, T_{pc}) and 58°C (melting temperature, T_m) allowing a high molecular diffusivity via increasing concentration of trans isomers and molecular jumps from one diagonal position of the cubic structure to another [6–8]. Because of its low T_m -value, high dielectric constant (~ 55) and waxy nature, succinonitrile also acts as a solid solvent/plasticizer to prepare redox-couple solid or gel electrolytes for dye-sensitized solar cells. Until now, succinonitrile has been used either with an ionic liquid [9–19], an organic iodide salt [13,14,20], an inorganic iodide salt [19], or with a polymer matrix [21–29] in the following composition: SN (with or without a polymer matrix)-XI-I₂. Here, the notation, X,

* Corresponding author.

E-mail address: rgupta@ksu.edu.sa (R.K. Gupta).

Utilization of poly(ethylene terephthalate) waste for preparing disodium terephthalate and its application in a solid polymer electrolyte

Nazrul Haq,¹ Faiyaz Shakeel,¹ Fars K. Alanazi,¹ Hamid Shaikh,² Idriss Bedja,³
Ravindra Kumar Gupta ³

¹Kayyali Chair for Pharmaceutical Industry, Department of Pharmaceutics, College of Pharmacy, King Saud University, P.O. Box 2457, Riyadh 11451, Saudi Arabia

²SABIC Polymer Research Center, Department of Chemical Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

³Cornea Research Chair, Department of Optometry, College of Applied Medical Sciences, King Saud University, P.O. Box 10219, Riyadh 11433, Saudi Arabia

Correspondence to: R. K. Gupta (E-mail: rgupta@ksu.edu.sa)

ABSTRACT: A widespread application and nonbiodegradability of the poly(ethylene terephthalate) (PET) have created a huge amount of waste, which is imposing a serious life-threatening environmental problem. In this study, we have utilized the PET waste to synthesize disodium terephthalate (DST), an organic salt having two Na⁺ ions per molecule. The purity of the DST phase was confirmed by Fourier transform infrared spectroscopy, X-ray diffractometry (XRD), and thermogravimetric analysis (TGA). A new poly(ethylene oxide)–DST polymer electrolyte was synthesized for utilizing Na⁺ ions of the DST. The electrical conductivity of the electrolyte was optimized by varying the [O]/[Na⁺] mole ratio with temperature and the results were explained using the XRD and differential scanning calorimetry studies. The TGA study showed that the electrolyte is thermally stable up to 200 °C. © 2019 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2019**, 136, 47612.

KEYWORDS: disodium terephthalate; electrical conductivity; polyethylene terephthalate waste; sodium ion; solid polymer electrolyte

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INTRODUCTION

Poly(ethylene terephthalate) (PET) belongs to the thermoplastic polymer of the polyesters, which is prepared industrially using terephthalic acid (TPA; C₆H₄[COOH]₂).¹ The PET is widely consumed in synthetic fibers; liquid refreshment, foodstuff, and other containers; thermoforming purpose; and engineering plastics. A widespread application and nonbiodegradability of the PET create a huge amount of waste. Most of the times, the Municipal solid waste containing a significant amount of waste plastics is incinerated in an open field, which releases toxic substances like dioxins, furans, mercury, and polychlorinated biphenyls into the atmosphere. These toxic substances are posing a threat to the health of living bodies, such as plants, animals, and human. Hence, a sustainable step toward a cleaner and healthier environment needs immediate attention of the environmentalists and scientists. In order to save our world, it is now necessary to develop new recycling technologies and waste disposal procedures, which should be also compatible with our socioeconomic aspects.¹ Till

now, numerous approaches of the polymer reprocessing and reutilization have been projected, among them, a chemical method is found the most beneficial in terms of economic and environmental issues.^{2,3}

A sodium ion conducting rechargeable battery has recently been considered as a promising candidate for next-generation battery, largely because of its high energy density and nontoxicity of sodium compounds.^{4–10} The natural abundance of sodium resources also makes a sodium ion battery economically cheap and viable. A solid-state battery is fabricated by sandwiching a Na⁺ ion conducting solid electrolyte between anode and cathode materials. Disodium terephthalate (DST) is considered as an anode material of sodium ion batteries.^{11–16} The DST is a salt derivative of the terephthalic acid, where H atom of hydroxyl radical is replaced by Na atom.^{17,18} Figure 1 shows its chemical structure. It has a crystal structure of a primitive orthorhombic unit cell with Pbc2₁ space group.¹⁷ This was prepared using the TPA with sodium hydroxide (NaOH) in aqueous condition.^{11,14,17,18}

N. Haq, H. Shaikh, and R. K. Gupta contributed equally to this article.

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Understanding the Electrical Transport–Structure Relationship and Photovoltaic Properties of a [Succinonitrile–Ionic Liquid]–LiI–I₂ Redox Electrolyte

Ravindra Kumar Gupta,* Hamid Shaikh, and Idriss Bedja

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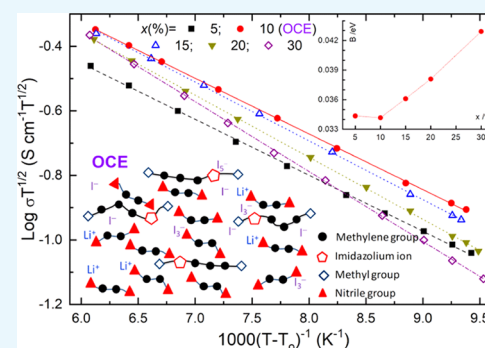


Article Recommendations



Supporting Information

ABSTRACT: The properties of succinonitrile-based electrolytes can be enhanced by the addition of an ionic liquid (IL). Here, we have reported the relationship between the electrical transport properties and the structure of a new [(1 - *x*)succinonitrile:*x*IL]–LiI–I₂ electrolyte, where the mole fraction (*x*) of the IL (1-butyl-3-methyl imidazolium iodide) was varied from 0 to 40%. Compositional variation revealed the optimum conducting electrolyte (OCE) at *x* = 10 mol %, possessing an electrical conductivity ($\sigma_{25^\circ\text{C}}$) of $\sim 7.5 \text{ mS cm}^{-1}$ with an enhancement of $\sim 369\%$. The partial replacement of succinonitrile by the IL eliminated the abrupt change in the slope of the $\log \sigma$ vs T^{-1} plot at the melting temperature of the succinonitrile–LiI–I₂ system, showing the Vogel–Tamman–Fulcher-type behavior owing to molecular chain disorder. Raman spectroscopy showed the I₃[−] concentration nearly twice the I₅[−] concentration for the OCE. Vibrational spectroscopy exhibited red shifts in the $\nu_{\text{C}\equiv\text{N}}$, ν_{CH_2} , $\nu_{\text{a,CC}}$, $\nu_{\text{a,N-CH}_3}$, and $\nu_{\text{s,N-butyl}}$ modes, indicating an interaction between succinonitrile and the IL. The area ratio $A_{\text{CH}_2}/A_{\text{C}\equiv\text{N}}$ increased slightly for *x* = 10 mol % (OCE) and largely for *x* > 10 mol %, indicating an increase in the C–H bond length. These observations indicated that the interaction between succinonitrile and the IL was enhanced at *x* > 10 mol %, which decreased the electrical conductivity of these electrolytes. Owing to fast ion transport, an OCE-based dye-sensitized solar cell showed a 40–55% decrease in the charge-transfer and Warburg resistances, resulting in ~ 139 and $\sim 122\%$ increases in J_{SC} and η , respectively.



INTRODUCTION

Research on solar cells as renewable energy sources is of current importance because of several environmental issues.¹ The availability of large amounts of solar irradiance along the Tropic of Cancer, which passes through countries like Algeria, Libya, Egypt, Saudi Arabia, and India, is also advantageous.¹ As a third-generation solar cell, the dye-sensitized solar cell (DSSC)—also called the Gratzel cell—is striking in terms of its simple cell structure, cost-effective materials and manufacturing processes, short energy payback time (<1 year), ability to capture light from all incident angles, and enhanced performance under real outdoor conditions.² However, DSSCs require an electrolyte with fast ion conduction (i) to inhibit back electron transfer reactions, (ii) to regenerate dyes via the oxidation of I[−] into I₃[−] at the working electrode, and (iii) to reduce I₃[−] into I[−] at the counter electrode.^{2,3} Using a liquid electrolyte consisting of 0.6 M 1-methyl-3-butyl imidazolium iodide, 0.03 M iodine, 0.1 M guanidinium thiocyanate, and 0.5 M *tert*-butylpyridine (TBP) in a 15:85 (v/v) mixture of valeronitrile and acetonitrile, Nazeeruddin et al.⁴ reported a cell efficiency (η) of 11.2% at 1 sun. Chiba et al.⁵ used a liquid electrolyte of 0.6 M dimethyl propyl imidazolium iodide, 0.1 M LiI, 0.05 M iodine, and 0.5 M TBP in acetonitrile to achieve a

certified cell efficiency of 11.1% at 1 sun. The addition of the ionic liquid (IL) helped increase the electrical conductivity and decrease the solvent evaporation rate. However, as solvent-based cells are prone to leakage, especially at elevated operating temperatures ($\sim 80^\circ\text{C}$) owing to the increased internal pressure, strong hermetic sealing is required.

Wang et al.⁶ synthesized a solvent-free electrolyte using the IL *N*-methyl-*N*-butylpyrrolidinium iodide and I₂ in succinonitrile (SN; $\text{N} \equiv \text{C}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{N}$). This electrolyte exhibited an electrical conductivity ($\sigma_{25^\circ\text{C}}$) of 3.3 mS cm^{-1} and apparent diffusion coefficients of 3.7 and $2.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for I[−] and I₃[−], respectively. The properties of this electrolyte were better than those of a gel electrolyte containing an IL, iodine, a solvent, and a gelator.⁷ This superior performance was attributed to the solid solvent/plasticizing properties of SN, which is a nonionic and low-molecular-weight plastic crystal

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