



Use of deep eutectic solvents in environmentally-friendly dye-sensitized solar cells and their physicochemical properties: A brief review

Journal:	<i>RSC Advances</i>
Manuscript ID	RA-REV-03-2024-001610.R2
Article Type:	Review Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Pishro, Khatereh A.; UNESP IBILCE, Chemistry and Environmental Science Gonzalez, Mario; UNESP, Chemistry and Environmental Science
Subject area & keyword:	Electrochemistry for energy < Energy chemistry

SCHOLARONE™
Manuscripts

Use of deep eutectic solvents in environmentally-friendly dye-sensitized solar cells and their physicochemical properties: A brief review

Khatereh A. Pishro^a, Mario Henrique Gonzalez^{a*}

^a São Paulo State University (UNESP), National Institute for Alternative Technologies of Detection, Toxicological Evaluation and Removal of Micropollutants and Radioactives (INCT-DATREM), Department of Chemistry and Environmental Science, São José do Rio Preto, SP, 15054-000, Brazil

*Corresponding author. Tel./Fax: +55 17 32212512

E-mail address: mario.gonzalez@unesp.br (M. H. Gonzalez)

Abstract

A novel way to mitigate the greenhouse effect is to use dye-sensitized solar cells (DSSCs) to convert carbon dioxide from the air into useful products, such as hydrocarbons, which can also store energy from the sun, a plentiful, clean, and safe resource. The conversion of CO₂ can help reduce the impacts of greenhouse gas emissions that contribute to global warming. However, there is a major obstacle in using DSSCs, since many solar devices operate with organic electrolytes, producing pollutants including toxic substances. Therefore, a key research area is to find new eco-friendly electrolytes that can effectively dissolve carbon dioxide. One option is to use deep eutectic solvents (DESs), which are potential substitutes for ionic liquids (ILs) and have similar advantages, such as being customizable, economical, and environmentally friendly. DESs are composed of low-cost materials and have very low toxicity and high biodegradability, making them suitable for use as electrolytes in DSSCs, within the framework of green chemistry. The purpose of this brief review is to explore the existing knowledge about how CO₂ dissolves in DESs and how these solvents can be used as electrolytes in solar devices, especially in DSSCs. The physical and chemical properties of the DESs are described, and areas are suggested where further research should be focused.

Keywords: Green solvents, solubility of CO₂, renewable technologies, electrolyte, dye-sensitized solar cells.

List of Abbreviations:

ILs-Ionic liquids

DES-Deep Eutectic Solvents

HBD-Hydrogen Bond Donor

HBA-Hydrogen Bond Acceptor

DSSCs-dye-sensitized solar cells

EC-Electrochemical Cell

PCEs-Power Conversion Efficiencies

VOCs-Volatile Organic Compounds

ChCl-Choline Chloride

EG-Ethylene Glycol

EmimI-1-ethyl-3-methylimidazolium

Reline-choline chloride and urea

I_{sc}-short circuit current

V_{oc}- open circuit Voltage values

PSCs-Perovskite Solar Cells

I⁻/I₃⁻-iodide/triiodide

TiO₂-Titanium dioxide

NADES-Natural Deep Eutectic Solvents

ECs-Electrochemical Capacitors

F.E.-Faradaic Efficiencies

MEA_{HCl}-monoethanolamine hydrochloride

MDEA-methyldiethanolamine

DMF-dimethyl formamide

IM-incorporating imidazole

FTO-Fluorine-doped tin oxide

FF-Fill Factor

LUMO-lowest unoccupied molecular orbital

HOMO-highest occupied molecular orbital

Eg-band gap

[PMIM]I- 1-propyl-3-methylimidazolium iodide

IPCE-Incident Photon-to-Current Conversion Efficiency

ACN-acetonitrile

EMIM-1-Ethyl-3-Methylimidazolium iodide

MEA.Cl- Ethylamine hydrochloride

DBN- 1,5-Diazabicyclo[4.3.0]-non-5-ene

DBU- 1,8-diazabicyclo- [5.4.0]undec-7-ene

TBAB -Tetrabutylammonium Bromide

MTPPBr- Methyltriphenylphosphonium Bromide

BMIMCl -1-Butyl-3-methylimidazolium Chloride

MEA-Monoethanolamine

MDEA-Methyldiethanolamine

[bmim][tf2N]- 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

KI-Potassium iodide

LiI-Lithium iodide

NaI-Sodium iodide

Fr-Fructose

Glu-Glucose

MA-Malonic acid

Gly-Glycerol

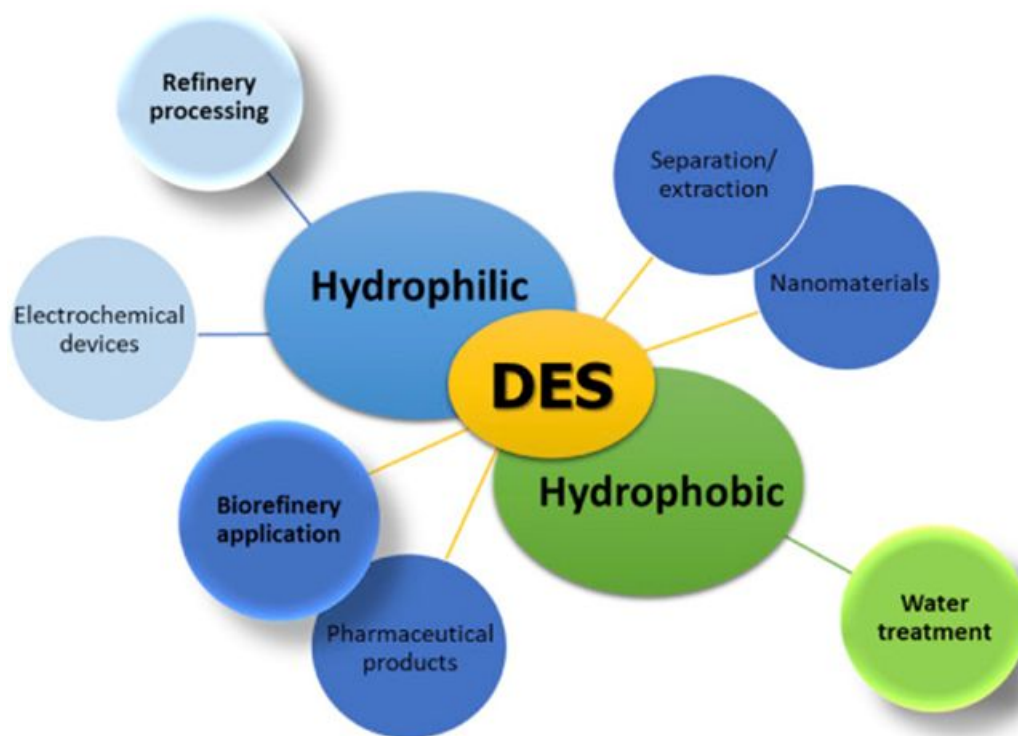
VOC-Volatile Organic Compound

1. Introduction

One of the most important challenges in recent years concerns the design of alternative renewable energy technologies that can replace fossil fuels and reduce their environmental damage^{1, 2}. According to the Paris Agreement, urgent actions are needed to lower the emissions of CO₂ into the atmosphere, as they cause serious effects in the environment³. One promising solution is to use solar cells to convert CO₂ into valuable products such as hydrocarbons, which can also store solar energy, a plentiful, clean, and safe resource⁴. The conversion of CO₂ can help reduce greenhouse gas levels, while at the same time absorbing sunlight, contributing to mitigating global warming⁵.

Artificial photosynthetic systems are devices that use sunlight as an energy source and water as an electron source to convert CO₂ into useful chemicals (fuels or carbohydrates). This can be achieved by combining a photovoltaic (PV) cell that generates electrons and holes with an electrochemical cell (EC) that oxidizes water at the anode and reduces CO₂ at the cathode⁶⁻⁸. An electrolyte is a vital component in these devices, as it enables charge transport between the electrodes. Most of the electrolytes used are non-aqueous, including polar organic solvents (acetonitrile, valeronitrile, and others) and green solvents (ILs and DESs)^{9, 10}. Ionic liquids (ILs) and deep eutectic solvents (DESS) have been proposed for various industrial processes and applications, such as chemical synthesis¹¹, absorption¹², biomass pretreatment¹³, extraction¹⁴,

electrolytes for electrochemistry (fuel cells and lithium batteries)¹⁵, and dye-sensitized solar cells (DSSCs)¹⁶⁻¹⁸. Scheme 1 provides an overview of DES applications, based on their hydrophilic and hydrophobic characteristics¹⁹.



Scheme 1. DES applications according to their individual hydrophilic and hydrophobic characteristics¹⁹.

Among the various technologies for converting solar energy, DSSCs offer the greatest potential for improving their properties, in terms of both environmental sustainability and energy conversion performance. DSSCs are a type of thin-film solar cell that has been widely studied for more than two decades, due to their simple preparation methodology, low toxicity, and low cost of preparation, and ease of production²⁰⁻²⁴.

DSSCs are based on a photoactive anode with an n-type semiconductor layer (usually TiO_2) sensitized by an organometallic dye, a counter electrode, and a liquid electrolyte that completes the circuit and regenerates the dye. Liquid electrolytes²⁵ have achieved a record efficiency of 14.7% and liquid DSSCs are low-cost solar cells with high power conversion efficiencies (PCEs). However, acetonitrile-based electrolytes and some other organic components used for DSSCs are harmful, while their volatility limits their performance and stability. To overcome this problem,

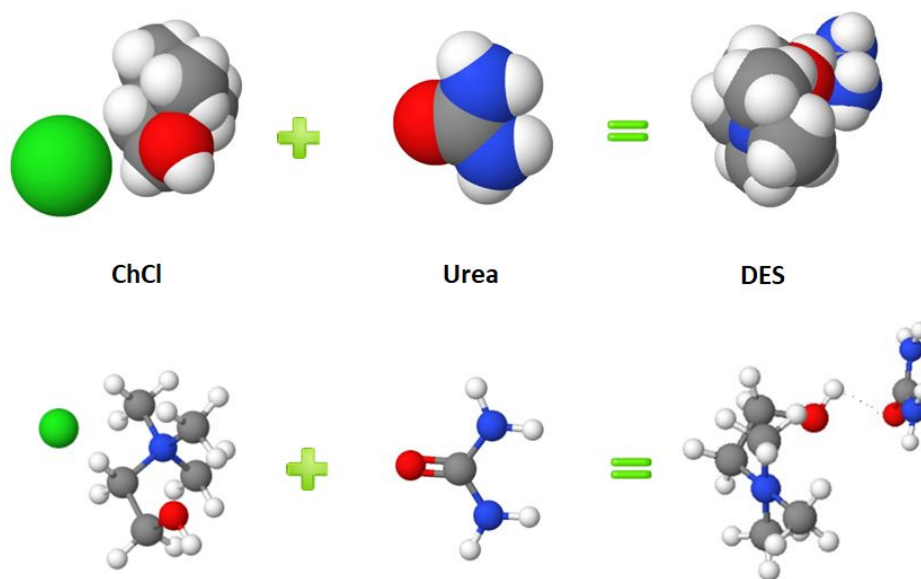
the use of DESs has been suggested as an attractive way to improve liquid electrolytes, with the advantages of low toxicity, biodegradability, high thermal stability, non-flammability, no vapor pressure, and low production costs ^{18, 26-28}.

The primary objective of this review is to examine a range of deep eutectic solvents (DESs) for their potential as innovative electrolytes in solar cells²⁹, focusing on the synthesis and properties of DESs, with particular attention given to their physicochemical attributes that facilitate the conversion of CO₂ into value-added chemicals. The mechanism of these solar cells emulates the natural photosynthesis process and is termed “artificial photosynthesis” ^{30, 31}. The review also outlines prospective avenues for future research within this area.

2. Deep eutectic solvents (DESs)

2.1. DESs as green solvents

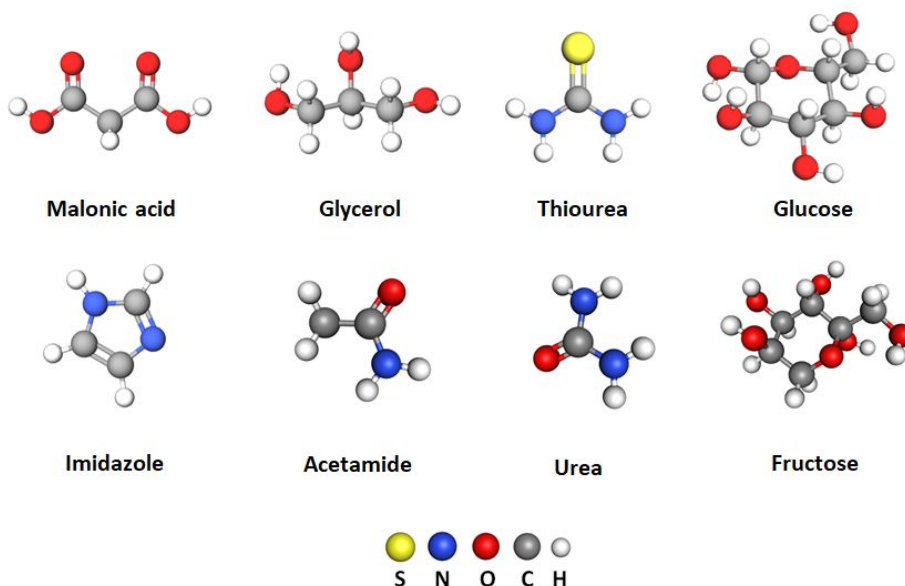
Green and sustainable solvents have influenced the recent development of the chemical industry. Volatile organic compounds (VOCs) are still widely used as solvents in industries, even though they are often toxic and highly flammable ^{32, 33}. Ionic liquids (ILs) are considered green solvents, due to their very low vapor pressure and high thermal stability, making them suitable for many processes. However, ILs have some drawbacks, such as high viscosity, high cost, and difficult synthesis ³⁴. Deep eutectic solvents (DESs) ^{35, 36} are new types of green solvents, usually composed of Lewis or Brønsted acids and bases, with a strong hydrogen bond network, where the interactions act to reduce the lattice energy. A simple preparation pathway for DESs using HBD and HBA is shown in Scheme 2 ³⁷. A DES is a binary or ternary mixture of safe and cheap components that include at least one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA), mixed in a specific molar ratio to form a eutectic mixture with a melting point much lower than that of any of the individual components ³⁸. The term “deep” should only be used for those mixtures with a eutectic point temperature much lower than that of an ideal liquid mixture, which explains the decreased melting point, compared to those of the individual components ^{39, 40}.



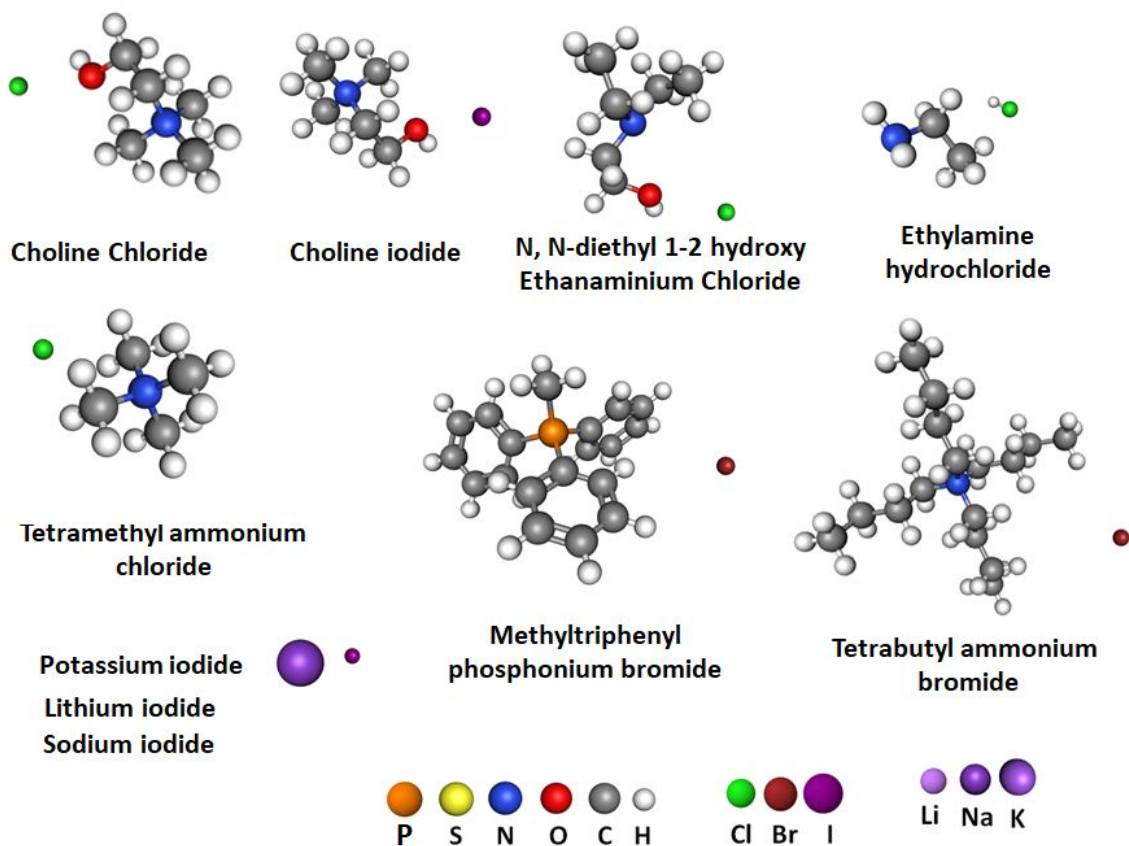
Scheme 2. A DES preparation pathway composed of HBD and HBA, with strong hydrogen bonds to reduce the lattice energy ³⁷.

Binary DESs are mixtures of one kind of HBA and one kind of HBD, while ternary DESs are mixtures of three components, which have also been reported in the literature ⁴¹. Some HBDs and HBAs used for the preparation of DESs introduced in this review are shown in Scheme 3.

Hydrogen Bond Donors (HBDs)



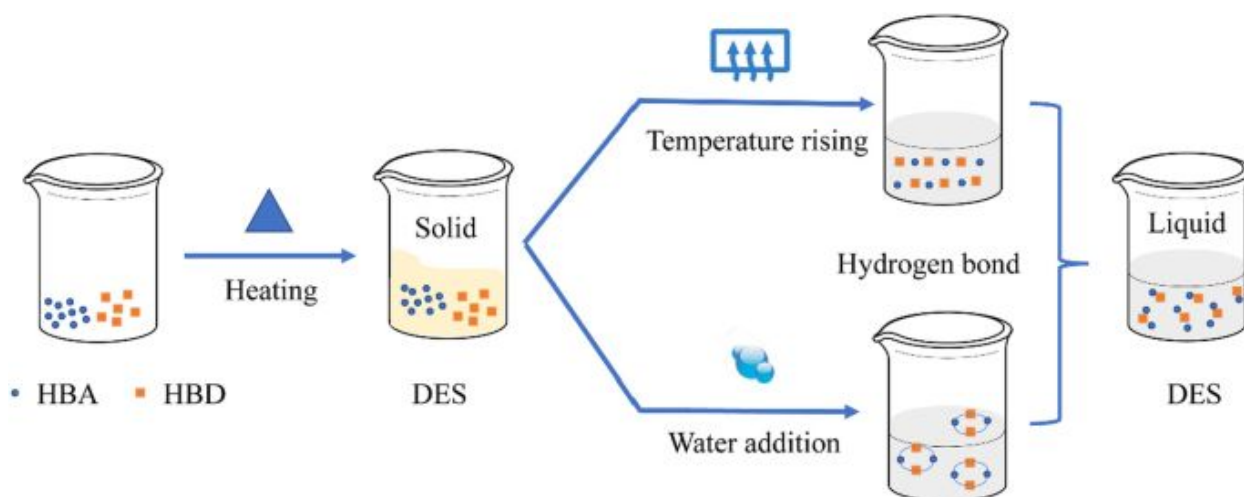
Hydrogen Bond Acceptors (HBAs)



Scheme 3. Some Hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) used in preparation of the DESs described in this review.

The electrolytes commonly used in DSSCs are non-aqueous polar solvents containing organic compounds (such as acetonitrile). However, these solvents are volatile and toxic, which poses environmental and safety risks. Therefore, there is a need to develop new “green solvents” that have similar physicochemical properties, but are eco-friendly and more sustainable. Among the candidates for green solvents are DESs, which are HBA and HBD combinations that form eutectic mixtures with low melting points. The physicochemical properties of DESs depend on the type and ratio of HBA and HBD, resulting in different interactions (such as hydrogen bonding, π - π bonding, or anion exchange)⁵¹. These interactions affect the density, viscosity, melting/freezing point, and conductivity of DESs, which are important factors influencing their performance as electrolytes in DSSCs. In addition, other properties such as thermal stability, toxicity, and biodegradability affect the application potential of DESs.

The various uses of DESs in scientific and industrial fields are determined by their performance, which is directly influenced by their physicochemical properties. The relationships between physicochemical properties, solvent performance, and applications of deep eutectic solvents are depicted in Scheme 4, where temperature and moisture expand the liquid range of DESs⁴².



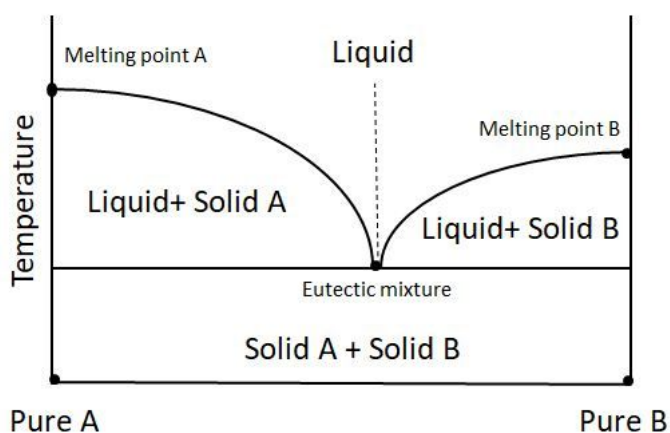
Scheme 4. The relationships between physicochemical properties, solvent performance, and applications of deep eutectic solvents⁴².

In the following subsections, the basic physicochemical properties of DESs for use as effective electrolytes in DSSCs will be discussed and compared.

2.2. Properties and characteristics of DESs

2.2.1. Melting point/freezing point

The melting point (mp) or freezing point (ΔT_f) of deep eutectic solvents is the property that defines the temperature at which the solid and liquid phases of the mixture are in equilibrium, which is much lower than those of their individual components, so they can form liquid mixtures at room temperature or below. The mp or ΔT_f of a DES is related to the strength of the interactions between the HBA and HBD structures and the medium that they are mixed with, such as water⁴³⁻⁴⁷, and depends on the type and ratio of the HBA and HBD components, as well as the interactions between them. The stronger the interactions, such as hydrogen bonds or Van der Waals forces, the lower the melting/freezing point of the DES. It is also possible to use a phase diagram to show the relationship between the composition and the melting/freezing point of a binary mixture of HBA and HBD. The lowest melting/freezing point is achieved at the eutectic point, where the HBA and HBD are mixed in a specific molar ratio that maximizes the interactions between them⁴⁸. Scheme 5 shows the theoretical phase diagram for binary HBD and HBA mixtures, which illustrates how the mp or ΔT_f of the DESs varies depending on the composition and ratio of the HBD and HBA.



Scheme 5. Eutectic point in a two-component (HBA and HBD) phase diagram³⁹.

The DES melting point influences the performance and stability of solar cells, as it affects the operating temperature range and the thermal degradation of the material ⁴⁹. The melting point of the DES, as well as the polarity, viscosity, and density of the solvent, all have an impact on the solubility of CO₂ in DESs. The CO₂ solubility in a DES is inversely proportional to the melting point of the DES. To obtain the correct melting point and solubility of CO₂ in DESs for solar cell applications, it is important to select a suitable mix and proportion of HBD and HBA. The DES melting point also affects the physical and chemical properties of the perovskite materials used in common types of solar cells. Perovskite materials have a crystal structure analogous to that of the mineral perovskite, composed of calcium, titanium, and oxygen (CaTiO₃). Increase of the heat treatment temperature can cause the absorption edge to present a red shift, the band gap to decrease, and the defect density of the perovskite material to increase. These changes can reduce the efficiency and stability of the solar cell. However, an appropriate heat treatment time and temperature can also passivate the defects and improve the solar cell performance ⁴⁹. It is important to adjust the melting point and the heat treatment conditions of the DES to optimize the properties of the perovskite material for solar cell applications.

2.2.2. Viscosity

Viscosity is a measure of the resistance of a fluid to flow. It is a property that determines the extent to which a fluid resists changing its shape or flowing. A fluid with high viscosity flows more slowly than a fluid with low viscosity, depending on its temperature, pressure, and composition.

The viscosity of DESs depends on the type and ratio of the HBD and HBA components, as well as the interactions between them. The stronger the interactions, such as hydrogen bonds or Van der Waals forces, the higher the viscosity of the DES. The viscosity of DESs affects their performance and applications in various fields, such as solar cells ⁵⁰, electrochemistry ⁵¹, catalysis ⁵², and biotechnology ⁵³. For example, the viscosity of DESs affects the solubility of CO₂ in them, which is an important factor for the conversion of solar energy and CO₂ to useful products such as hydrocarbons. The solubility of CO₂ in DESs decreases as the viscosity increases. Therefore, selecting the best mix and proportion of the HBD and HBA parts is important for achieving suitable CO₂ solubility and viscosity in DESs for solar cell uses.

The temperature and the ionic species in the DES electrolyte mixtures affect their viscosity, which is an indicator of the fluidity of the electrolyte. Dokohani et al. ⁵⁴ used a DES based on choline chloride and ethylene glycol (ChCl-EG), adding different iodide salts to obtain electrolytes for dye-sensitized solar cells (DSSCs). Measurements were made of the viscosity of these electrolytes with added KI, 1-ethyl-3-methylimidazolium (EmimI), or KI-EmimI, at 293–365 K, which showed that the viscosity decreased at higher temperatures, improving DSSC performance under solar irradiation. In addition, the viscosity varied with the composition of the iodide salt, where the electrolytes with smaller cations had higher viscosity. The molecular weight of the ionic species also influenced the viscosity of the electrolytes. The simulated viscosity of the KI-containing electrolyte was 27.71 mPa.s., which was close to the experimental value of 26.76 mPa.s. at 298 K. It was also found that the KI used in DES preparation enhanced the DSSC performance, but also increased the viscosity of the solution.

2.2.3. Density

The density (ρ) of a substance is a measure of the amount of mass (m) per unit volume (V). The density of a DES is an important physical property that affects its solvation ability, viscosity, thermal conductivity, and mass transfer. The density of a DES depends on several factors, such as the type and ratio of the components, the temperature, the water content, and the presence of other additives. The density of a DES influences its thermal conductivity, which is a measure of how well a material can transfer heat. A higher density means a higher thermal conductivity, as the molecules are closer together and can transfer heat more easily. However,

density is not the only factor affecting the thermal conductivity of a DES. The hydrogen bonding between the components and the interactions with other molecules, such as CO₂, also play a role. In some DESs, the addition of a salt or hydrogen bond donor enhances the thermal conductivity, which may be attributed to the fact that the effect of density is stronger than that of hydrogen bonds ⁵⁵. For example, at lower pressure, the ethylene glycol and CO₂ interaction dominates, while at a higher pressure, the chloride and CO₂ interaction is most important. Therefore, DESs offer the same advantages as the CO₂ absorbent in ionic liquids, while also exploiting a hydrogen bond donor ⁵⁶. The density of a DES affects its viscosity, which is a measure of how resistant a fluid is to flow. Higher density is associated with higher viscosity, as the molecules are more tightly packed and have more friction. However, the viscosity of a DES also depends on the temperature, the water content, and the hydrogen bonding between the components. For example, increasing the temperature or adding water can reduce the viscosity of a DES, as the thermal energy or the water molecules can disrupt the hydrogen bonds and increase the fluidity. The viscosity of a DES is an important factor for its application, because it determines the mixing and diffusion rates, the mass transfer coefficients, and the energy consumption ⁵⁷.

The density of a DES determines its solubility properties, which are crucial for its use as a solvent for various organic reactions. Higher density results in higher solubility of polar and ionic compounds, because the molecules can form stronger interactions with the solute. However, density is not the only factor that affects the solubilization capacity of a DES. The solvation behavior is also influenced by the polarity, hydrogen bonding, molecular size, and shape of the components, as well as the nature of the solute. For instance, in organic oxidation reactions, DESs can break down both lipophilic and hydrophilic organic species, making the oxidation of organic compounds by hydrogen peroxide more effective ⁵⁸.

DESs have been used as electrolytes for DSSCs, a type of low-cost and environmentally friendly photovoltaic device that uses a dye to absorb light and generate electricity. The density of a DES is one of the physical properties that affect its performance in this application. Different studies have investigated the effect of density on the performance of DSSCs with DES-based electrolytes. For example, one study used a DES composed of choline chloride and urea (Reline) ⁵⁹ as an electrolyte for carbon-based electrochemical capacitors. The study found that the specific capacitance increased from 100 to 157 F g⁻¹ at a 1 A g⁻¹ current load, by adding 1 wt.% water to the DES system, due to the decrease in viscosity and the increase in ionic conductivity ⁵⁹.

Another study used two DESs composed of choline chloride and ethylene glycol or urea as electrolytes for DSSCs. The device using choline chloride and ethylene glycol showed an increase in the short circuit current (I_{sc}) in opposite, the devices using choline chloride and urea electrolyte exhibited improved open circuit voltage values (V_{oc}).⁶⁰, due to the different molecular structures and the ways that the DES parts interacted with the dye and the redox mediator.

2.2.4. Conductivity

DESs carry electric charges due to their conductivity, which is an important property for their application as electrolytes in solar cells, since it influences the performance and speed of the electrochemical reaction that occurs in the solar cell. Factors including the type and ratio of the components, temperature, water content, and the presence of other additives affect the conductivity of a DES. The viscosity, polarity, hydrogen bonding, and ionic strength of the liquid can also affect the conductivity of a DES. For example, the conductivity of some DESs can be increased by adding water or salts, resulting in lower viscosity and increase of the number of charge carriers⁶¹.

Various studies have explored how conductivity affects solar cells with electrolytes based on DESs. For instance, one study used a choline chloride and ethylene glycol DES as an electrolyte for DSSCs and found that the DSSCs with the DES electrolyte exhibited higher power conversion efficiency, compared to DSSCs with a traditional liquid electrolyte, because the DES had higher conductivity and a lower recombination rate⁶². Investigation was made of perovskite solar cells (PSCs), a new and efficient type of photovoltaic device that uses a perovskite material to absorb light and transport charge, using a DES composed of choline chloride and urea as the electrolyte. It was found that PSCs with the DES electrolyte had better open-circuit voltage and fill factor, compared to PSCs with a usual solid-state electrolyte, because the DES provided higher conductivity and a smoother interface⁶².

The conductivity of DESs is affected by temperature, the alkyl chain length of the cation, the HBD to HBA molar ratio, and viscosity. For instance, adding a 33% mole fraction of choline chloride to a DES based on choline chloride and glycerol increased its conductivity from 1.047 to more than 1 mS/cm⁶³, with the DES conductivity being slightly affected by the cation alkyl chain length. In addition, the conductivity of DESs increases with temperature, because the hydrogen bond network breaks and the ionic mobility increases⁶⁴.

Viscosity affects the conductivity of DESs, with higher viscosity leading to lower conductivity, and for some electrochemistry applications, the conductivity of DESs should not be too low (lower than 1 mS cm^{-1} at ambient temperature) ⁶⁵. Hence, DESs are a good choice for electrochemical applications, including as electrolytes for solar cells, because they have low viscosity and high conductivity ^{63, 66}.

2.2.5. Acidity

Acidity is an important parameter affecting the characteristics of new solvents. The Brønsted acidity of DESs can be determined by measuring the pH or the Hammett acidity function, while the Lewis acidity can be evaluated by FT-IR analysis ^{67, 69}. The acidity of a DES is a property that affects its ability to act as an electrolyte in solar cells, since it can influence the electrochemical reactions that occur in the cell, as well as the stability and performance of the device. If the acidity level changes, it can change the redox potential of the mediator, which in DSSCs is usually iodide/triiodide (I^-/I_3^-). The redox potential of the mediator determines the open-circuit voltage of the DSSC, which is a measure of the maximum voltage that the device can produce. A higher redox potential result in a higher open-circuit voltage and higher power conversion efficiency.

The acidity of the DES can affect the redox potential of the mediator by changing the equilibrium between I^- and I_3^- . Higher acidity, with lower pH, favors the formation of I_3^- and increases the redox potential ⁵⁹. Another way that acidity affects the DES electrolyte is by influencing the stability and corrosion of the electrode materials and the dye sensitizer. The electrode materials are usually titanium dioxide (TiO_2) for the photoanode and platinum (Pt) for the counter electrode. The dye sensitizer is usually a ruthenium complex that absorbs light and injects electrons into the TiO_2 . The acidity of the DES can affect the stability and corrosion of these materials by changing the chemical reactions that occur on their surfaces. At higher acidity, there is a higher concentration of protons (H^+) available to react with the electrode materials and the dye sensitizer, leading to degradation or dissolution. For example, higher acidity can cause the oxidation of Pt to PtO or PtO_2 , which reduces the catalytic activity of the counter electrode ⁶⁹. Higher acidity can also break down the ruthenium dye, which makes the photoanode less effective in absorbing light and injecting electrons ⁶⁹. Furthermore, higher acidity can cause hydrolysis of the ruthenium dye, which reduces light absorption and the electron injection

efficiency of the photoanode ⁷⁰. Therefore, the acidity of the DES electrolyte is an important factor affecting the performance and durability of the solar cell. The optimal acidity of the DES electrolyte depends on the type and composition of the DES, the type and concentration of the mediator, and the type and structure of the electrode materials and the dye sensitizer. The acidity of the DES electrolyte can be adjusted by changing the ratio of the hydrogen bond donor (HBD) and the hydrogen bond acceptor (HBA) in the DES, or by adding water or other additives to the DES ^{71, 72}.

2.2.6. Hydrophobicity and hydrophilicity

The hydrophobicity and hydrophilicity of DESs are important factors that affect their performance as electrolytes in solar cells. Hydrophilic DESs are water-miscible and can be used to improve the thermophysical properties of the electrolyte solution. The hydrophobicity and hydrophilicity of DESs depend on the components and the molar ratio of the hydrogen bond donor and acceptor. For example, tetrabutylammonium chloride and decanoic acid form a hydrophobic DES, while choline chloride and urea form a hydrophilic DES. Molecular dynamics simulations can be used to study the interfacial properties of hydrophobic DESs with water, including interfacial tension, solubility, and hydrogen bonding ⁷². The hydrophobicity and hydrophilicity of DESs can also affect the processing of functional composite resins, such as epoxy, phenolic, acrylic, polyester, and imprinted resins, by modifying their properties, enhancing their recyclability, and endowing them with functionality ⁷³. Various methods such as contact angle and surface tension measurements, partition coefficient determination, and fluorescence spectroscopy can be used to evaluate the hydrophobicity and hydrophilicity of DESs ⁷⁴. These methods can help in the design and optimization of DESs for specific applications in solar cells and other fields. A variety of DSSC devices can be obtained using either hydrophilic or hydrophobic DESs ^{16, 47}. An aqueous choline chloride-based DES solution was utilized as an efficient electrolyte in DSCCs ⁶⁰, leading to enhancements of the cell parameters and increasing the overall power conversion efficiency (PCE) to nearly 2%. Such performance is on a par with the PCEs of mid-to-high-tier water-based DSSCs.

2.2.7. Volatility

Volatility is a property that measures the tendency of a substance to evaporate. The volatility of the electrolytes used in solar cells can affect performance and durability, since it can cause leakage, corrosion, degradation, and efficiency loss. When used as electrolytes, DESs have the advantages of low volatility, high conductivity, good solubility of CO₂, and low toxicity. Such DESs can be obtained using hydrogen bond donor and acceptor mixtures such as choline chloride and urea, or choline chloride and ethylene glycol, for application as electrolytes in low-cost and high-efficiency DSSC photovoltaic devices. DESs can improve the electrochemical properties of DSSCs, such as the open circuit voltage, the short circuit current, and the impedance, in addition to being environmentally friendly, biodegradable, and easy to prepare ^{59, 60, 75, 76}.

2.2.8. Surface tension

Surface tension is a property that measures the force that acts on the surface of a liquid, making it behave like an elastic membrane. The surface tension of the electrolytes used in solar cells can affect the formation and stability of the interface between the electrolyte and the electrodes, as well as charge transfer and electron recombination. In addition to high conductivity, good solubility of CO₂, and low toxicity, DESs have low surface tension, contributing to improvement of the electrochemical properties of DSSCs, such as the open circuit voltage, the short circuit current, and the impedance ^{59, 77, 78}.

3. Preparation of DESs

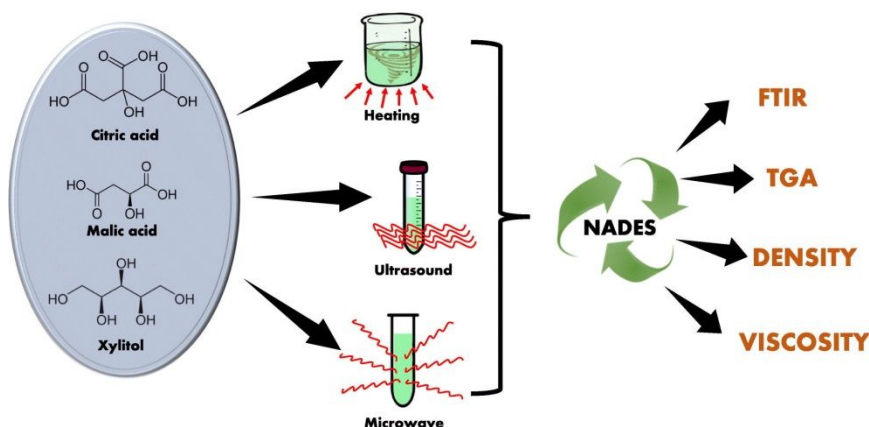
3.1. Selection of HBDs and HBAs

The main methods described in the literature for synthesis of DES are based on stirring and heating, freeze drying, evaporation, and microwave-assisted synthesis ⁷⁹. The most popular method involves mixing and heating two or three components, until a homogeneous liquid is formed ⁸⁰. Among the different components used in the mixture, attention is increasingly being focused on those suitable for the synthesis of hydrophobic DESs that are stable in the aquatic environment ^{43, 46}. The DES type Cat⁺X⁻ + zRZ, such as ChCl⁺urea, is especially popular due to its hydrophobicity

and stability in aqueous mixtures⁴³. The ultrasound-assisted and microwave-assisted DES synthesis techniques are faster and more efficient than the use of stirring and heating at 50 °C. However, the stirring and heating synthesis method has the advantages of simplicity and the ability to produce larger volumes of solvents⁸¹. The formation of a eutectic solvent occurs due to hydrogen bonding of the precursors, together with intermolecular interactions involving Van der Waals and electrostatic forces between HBDs and HBAs. The NMR and FTIR spectra of the synthesized DES show bands typical of the functional groups of the precursors that were used.

The selection of HBDs and HBAs is based on the desired properties of the DESs, including aspects such as solubility, conductivity, viscosity, surface tension, volatility, toxicity, and biodegradability. Certain HBDs and HBAs are mixed together in a fixed molar ratio to make Natural Deep Eutectic Solvents (NADES), which are a type of eutectic mixture. These solvents are considered “natural” because their constituents are naturally found in plants. The main components of NADES include sugars, organic acids, bases, and amino acids^{79,86}. The introduction of ultrasound and microwave-assisted synthesis methods⁸¹ resulted in a faster and more efficient process, while the stirring and heating methods enabled the production of larger volumes of solvents. Infrared spectroscopy (ATR-FTIR) and thermogravimetric analysis (TGA) were used to characterize the prepared NADES and identify intermolecular interactions⁸¹. Hydrogen bonds were observed between the precursor molecules, regardless of the synthesis method, and they revealed interactions between the precursor components and decomposition temperatures exceeding 150 °C⁸¹.

The scheme 6 demonstrates that various synthesis methods can yield NADES with consistent properties, despite differences in efficiency and equipment requirements. Researchers can choose the most suitable method based on their specific needs and constraints, and all synthesis methods yield NADES with similar physicochemical characteristics⁸¹.



Scheme 6. The synthesis of NADES using different methods⁸¹.

Examples of HBAs are choline chloride, ethylamine hydrochloride, tetramethylammonium chloride, tetrabutylammonium chloride, N, N-diethyl 1-2 hydroxy ethanamidium chloride, and methyltriphenylphosphonium bromide, while examples of HBDs are malonic acid, citric acid, acetic acid, Urea, thiourea, glycerol, ethylene glycol, acetamide, fructose, glucose, benzamide and imidazole. Some of the HBDs and HBAs structures presented in this review are depicted in Scheme 2. The choice of the HBDs and the HBAs also depends on the application of the DESs, for example, as catalysts, solvents, electrolytes, or extraction agents⁸²⁻⁸⁴, in addition to the nature of the analyte to be evaluated or determined.

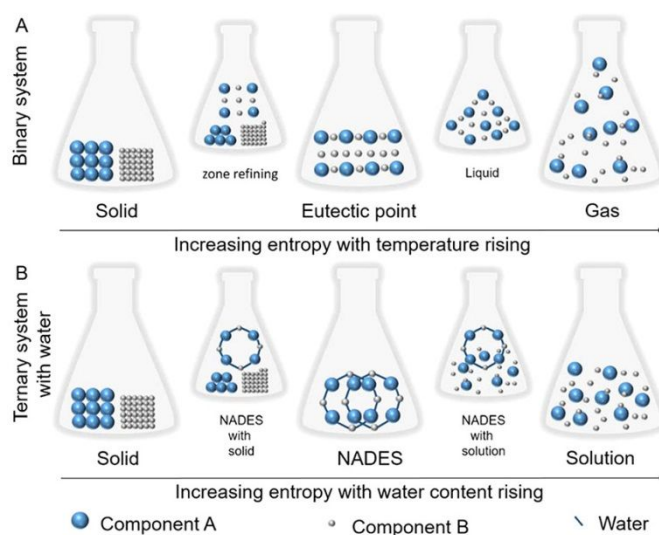
3.2. Biodegradability and low toxicity of DESs

DESs are a class of alternative electrolytes that have low toxicity and high biodegradability, which makes them suitable for use as electrolytes in solar cells. DESs are formed by mixing a hydrogen bond donor and acceptor, usually derived from biological sources such as carboxylic acids, alcohols, amines, amides, and ammonium salts. The toxicological properties of DESs depend on the components used, so the choice of benign materials can produce solvents with low toxicity. In addition, microorganisms easily biodegrade DESs, reducing the environmental impact of the waste generated. DESs can improve the performance and durability of solar cells, as they

offer a stable electrochemical window, good solubility of CO₂, low surface tension, and high conductivity^{59, 85}.

As petroleum resources are dwindling worldwide, future work should focus on exploring the potential of using DESs as new “green” media for solar devices, fully replacing the hazardous and toxic VOCs that are still widely used. As discussed, many components of DESs are from natural sources^{86, 87}, leading to the introduction of natural deep eutectic solvents (NADES) that present extremely low toxicity and high biodegradability.

Entropy plays a crucial role in NADES formation; when components are mixed in the right proportion, their molecular interactions lead to a decrease in entropy, resulting in an eutectic point. Heating is often employed during NADES preparation; it aids in dissolving the components and promotes molecular interactions and eutectic formation. As scheme 7 demonstrates, when entropy rises, the strength of intermolecular bonding decreases, which subsequently impacts the relevant physical parameters⁸⁶.



Scheme 7. Kinetic energy models for a binary NADES (A. temperature administration and B. water content administration)⁸⁶.

3.3. Adding water to DESs

The addition of water to DESs used as electrolytes in solar cells can affect their conductivity and stability. Water can increase ion mobility and enhance the conductivity of DES electrolytes, resulting in improved performance of the solar cell ⁵⁹. The substance Reline, composed of choline chloride (HBA) and urea (HBD), serves as one example. Electrochemical capacitors can use Reline as a green electrolyte to store electrical energy. Adding 1 wt.% water to Reline can increase the specific capacitance from 100 to 157 F g⁻¹ at a 1 A g⁻¹ current load. This means that more charge can be stored per unit mass. The addition of water can strengthen the hydrogen bonds between the NH and OH groups of the HBD molecules, which can enhance the charge transfer process. Another example of a DES is the mixture of choline chloride and lactic acid, which can also be used as an electrolyte for electrochemical devices. Adding water to this DES does not affect the interactions between the HBA and HBD molecules, but instead forms solvated clusters of the DES. This may affect the diffusion and mobility of the ions in the electrolyte, as well as the stability of the electrode materials ⁸⁸. However, excessive amounts of water can also cause phase separation and decrease the stability of the DES electrolyte, leading to reduced efficiency of the solar cell. Therefore, the effect of adding water to DESs used as solar cell electrolytes will depend on the type and composition of the DES, as well as the amount of water added. Water can modify the structure and dynamics of the DES molecules, which in turn can influence the performance and efficiency of the solar cell.

3.4. Solubility of CO₂ in DESs

The solubility of CO₂ in DESs is an important factor for using them as electrolytes in solar cells, as it affects the conductivity, stability, and performance of the devices. CO₂ is a greenhouse gas that solar cells can capture and utilize to produce electricity and reduce emissions. However, the solubility of CO₂ in DESs depends on several factors, such as the type and composition of the DES, the temperature and pressure of the system, and the presence of water or other additives.

The PC-SAFT equation of state has been used to estimate the solubility of CO₂ in 109 different DESs, covering a wide range of temperatures and pressures ⁸⁹. It was found that the PC-

SAFT model could provide accurate and reliable predictions of CO₂ solubility in DESs. It was also possible to propose generalized correlations to predict model parameters for new and upcoming DESs.

Amine-based DESs are a type of green and sustainable solvents that can be used as electrolytes for solar cells. Amine-based DESs consist of a hydrogen bond acceptor (HBA) that is typically an amine, together with a hydrogen bond donor (HBD) that is usually an organic acid or a salt. They have a low melting point, high solubility, and high conductivity, which are desirable properties for solar cell electrolytes. They can also capture and utilize CO₂, a greenhouse gas, to produce electricity and reduce emissions.

An amine-based DES used as a DSSC electrolyte was able to achieve a power conversion efficiency of 6.8%, comparable to that of a conventional ionic liquid electrolyte, with the additional advantages of high electrochemical stability and low viscosity, which are advantageous for DSSC performance⁵⁹. A mixture of choline chloride and urea is another example of an amine-based DES that can also serve as an electrolyte for electrochemical capacitors (ECs), which are devices that store electrical energy by accumulating charges on the electrodes. In another study, DESs⁶⁰ increased the specific capacitance and the voltage window of the ECs, enabling them to store more energy per unit mass and operate at higher voltages. It was also shown that adding a small amount of water to the DES could further enhance the charge transfer process and the cycle stability of the ECs.

Water is an eco-friendly and renewable solvent, but many reactions are slow in water. CO₂ has low solubility in water (0.033 M) under ambient conditions,⁹⁰ which limits the efficiency of its adsorption and conversion in solar cells. A common technique for CO₂ capture is using amine solvents, which have high selectivity and capacity, but also have drawbacks such as high corrosiveness⁹¹ and high energy consumption⁹², which hinders their use in solar cells^{93, 94}.

DESs have attracted attention in both experimental and theoretical studies, due to their ability to efficiently capture CO₂. In particular, a combination of ethanolamine hydrochloride (HBA) and tetraethylenepentamine (HBD) in a ratio of 1:9, referred to as EAHC-TEPA, showed remarkable CO₂ solubility, among several DESs investigated⁹⁵. Haider and Kumar⁹⁶ developed amine-based DESs with bulky structures that exhibited superior CO₂ uptake, while maintaining minimal CH₄ absorption, demonstrating a pronounced preference for CO₂.

Studies have explored the integration of CO₂ sequestration and transformation using amine-based solvents that can absorb CO₂ and serve as electrolytes for electrochemical conversion. Pérez-Gallent et al.⁹⁷ found that using both chemical and physical absorption solvents in combination led to high faradaic efficiencies (F.E.) of up to 50%, together with a 30% carbon conversion rate. An aqueous amine-based DES, [monoethanolamine hydrochloride][methyldiethanolamine] ([MEA·HCl][MDEA]), achieved a high F.E. of 71% for production of CO at a potential of -1.1 V vs. RHE at an Ag electrode, which was 33% higher than for [MEA·HCl][MEA]. Elsewhere, an innovative DES composed of choline chloride and ethylene glycol was utilized as an electrolyte in place of dimethyl formamide (DMF), enhancing the electrochemical CO₂ reduction efficiency, due to its favorable CO₂ solubility⁹⁸. In a similar vein, [MEA·HCl][MDEA], as a novel aqueous amine-based deep eutectic solvent, was formulated as an electrolyte for the reduction of CO₂ to CO, showing a high faradaic efficiency of 71% for CO production at -1.1 V vs. RHE at an Ag electrode, exceeding the performance of [MEA·HCl][MEA] by 33%⁹⁹.

Building on these studies, other work developed a DES by combining choline chloride and ethylene glycol, for use as an electrolyte¹⁰⁰. This new formulation replaced dimethylformamide (DMF) and contributed to advancements in DSSC technology, showing improved efficiency in the electrochemical reduction of CO₂, attributed to enhanced CO₂ solubility. Notably, the use of an Au electrode resulted in CO as the primary product, achieving a faradaic efficiency of 81.8%. Despite these findings, amine-based solvents remain the preferred choice for designing DESs with high CO₂ solubility.

In addition, imidazole and its derivatives have long been recognized as potent components in ionic liquids (ILs) and DESs for enhancing CO₂ solubility^{101, 102}. In a study examining the effects of modifying the imidazole substituent groups, considering the compounds 2-methylimidazole (2-MeIM), 2-ethyl-4-methylimidazole (2-Et-4-MeIM), and 1,2,4,5-tetramethylimidazole (1,2,4,5-MeIM), the addition of 2 M 1-propyl-3-methylimidazolium iodide ([PMIM]I) improved the capacity of the DESs to capture CO₂¹⁰³. Boualavong and Gorski¹⁰⁴ employed a chemical reaction equilibrium model to explore how variations in the substituent groups of imidazole affected CO₂ capture efficiency and energy requirements. The authors proposed a method to reduce the energy consumption of electrochemical capture technologies by doubling the number of CO₂ molecules captured per electron transferred.

Future research should address the existing gaps in assessment of the efficiency and energy requirements for solar cells incorporating imidazole (IM) or its derivatives such as 2-MeIM, 2-Et-4-MeIM, and 1,2,4,5-MeIM into the formulated DESs composed of hydrogen bond donors and acceptors. Table 1 shows some of the reported DESs prepared using different HBDs and HBAs, together with their solubilities at various temperatures and pressures.

Table 1. DESs prepared using different HBDs and HBAs, with their solubilities at different temperatures and pressures.

DES components and absorption conditions						
ILs/HBA	HBD	Molar ratio	Solubility (mol.mol ⁻¹)	T (K)	P (bar)	Reference
ChCl	Urea	1:1.5	0.201	313.15	118.4	¹⁰⁵
ChCl	Ethanolamine	1:6	0.0347	298	10	¹⁰⁶
ChCl	EG	1:2	0.5396l	303.15	58.6	¹⁰⁷
ChCl	Urea	1:2	0.6	303.15	60	¹⁰⁸
ChCl	TEG	4:1	0.0667	293	5	¹⁰⁹
ChCl	Lactic acid	1:2	0.0248	348	19.27	¹¹⁰
ChCl	Glycerol+DBN	1:2:6	0.111	Ambient	Ambient	¹¹¹
ChCl	Urea+water	50%	0.111	313	7.8	¹¹²
TBAB	Ethanolamine	1:6	0.0407	298	10	¹⁰⁶
MTPPBr	Ethanolamine	1:6	0.0518	298	10	¹⁰⁶
BMIMCl	MEA	1:4	0.214	Ambient	Ambient	¹⁰²
MEA.Cl	EDA	1:3	0.2698	Ambient	Ambient	¹¹³
TBAB	MDEA	1:4	0.29	303.15	10	¹¹⁴
[DETA][IM]	EG	1:2:2	0.2235	298.15	1.0	¹¹⁵
[bmim][tf2N]	DBU	1:1	1.0	298	1.0	¹¹⁶
ChCl	1,4-Butanediol	1:3	0.0164	298	5.14	¹¹⁷
ChCl	2,3-Butanediol	1:4	0.0188	298	5.08	¹¹⁷
ChCl	Glycerol	1:2	0.8589	303	58	¹¹⁸
TEG	DBU	1:1	1.04	298	1.0	¹¹⁹

As shown in Table 1, the solubility of CO₂ in DESs is influenced by both temperature and pressure. Generally, the solubility of a gas such as CO₂ decreases with increase in temperature and

decrease in pressure ¹²⁰. This is because higher temperatures provide more kinetic energy to the gas molecules, making them more likely to escape from the solvent. DESs, which are a type of ionic liquid, have been found to have good solubility for gases, including CO₂, which can be advantageous for applications such as in solar cells. The solubility is typically expressed as the mass of the gas per unit mass of solvent, at a given temperature and partial pressure of the gas ¹²¹. For solar cells, specifically DSSCs, DESs can be used as electrolytes. Researchers have developed choline chloride-based DESs as effective electrolytes for these types of solar cells. They offer benefits such as easy preparation, low cost, biodegradability, and non-toxicity, which are important for large-scale production and commercialization ⁶⁰.

The use of DESs as electrolytes in solar cells can potentially improve the open-circuit voltage and short-circuit current, depending on their molecular structures. This makes them an interesting area of research for enhancing the efficiency and eco-friendliness of solar cell technologies ⁶⁰. In particular, the CO₂ solubility in DESs can have significant implications for their use as green and sustainable electrolytes in solar cells. Amine-based DESs are promising candidates for solar cell electrolytes, offering benefits such as low cost, high efficiency, high stability, and environmental friendliness. However, understanding the underlying mechanisms and optimizing the properties and performance of these DESs requires further experimental and theoretical studies.

4. DESs as electrolytes in dye-sensitized solar cells (DSSCs)

4.1. Preparation of DSSCs and their advantages

DSSCs are devices that convert light into electrical energy by receiving photons from sunlight which excite the electrons of the dye molecule, and are then injected into the TiO_2 layer.

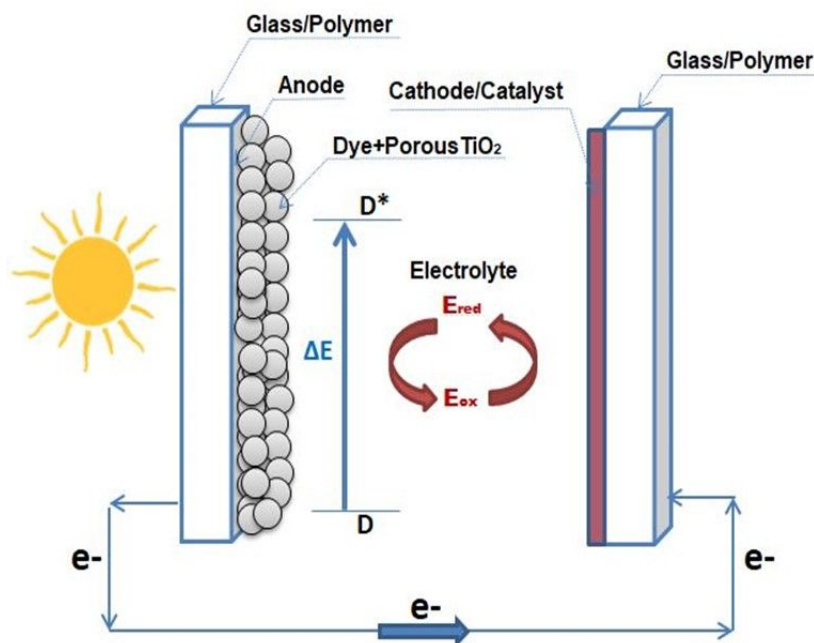
A DSSC (as shown in Scheme 8) classically consists of the following components ⁷⁸: (1) a photo-sensitized anode, usually made of a semiconductor material such as titanium dioxide (TiO_2), which has dye molecules on top of it that absorb sunlight and generate electrons; (2) an electrolyte that may be liquid or solid, usually possessing an iodide (I^-) and tri-iodide (I_3^-) couple that assists in moving electrons from the dye to the cathode; (3) a counter electrode, typically composed of platinum or other conductive material, which collects electrons and returns them to the electrolyte.

The iodide and triiodide ions constitute the redox couple commonly used in DSSC electrolytes, playing a crucial role in the operation of these solar cells by facilitating the transport of charge and contributing to the overall efficiency of the device. The iodide ion (I^-) acts as a charge carrier, while the triiodide ion (I_3^-) helps the oxidized dye molecules to regenerate, completing the electrical circuit of the cell ¹²². This redox couple is widely adopted due to its favorable recombination kinetics and ability to improve the performance of the solar cell.

The operation of a DSSC involves the dye molecules absorbing photons from sunlight and becoming excited, with subsequent injection of electrons into the conduction band of the semiconductor anode. From there, the electrons flow through an external circuit to do work (such as powering a device), before returning to the counter electrode. The redox mediator in the electrolyte then completes the circuit by regenerating the dye molecules.

The fabrication of DSSCs is mostly performed according to a well-established protocol ¹²³, to prevent metal contamination. The glass or Teflon containers are firstly cleaned with ethanol (EtOH) and a 10% hydrochloric acid (HCl) solution. Throughout the fabrication process, only plastic tools (such as spatulas and tweezers) are utilized. Fluorine-doped tin oxide (FTO) glass substrates are cleaned by immersion for 15 min in an ultrasonic bath with detergent, thorough rinsing with deionized water and EtOH, and exposure to a UV- O_3 for 18 min. The UV- O_3 method, which combines ultraviolet (UV) light and ozone (O_3) for surface cleaning and treatment, is particularly effective for removing organic contaminants from surfaces, without damaging the sample. After cleaning, the substrates are soaked for 30 min in a 40 mM TiCl_4 solution, at 70 °C,

followed by rinsing. A transparent layer of TiO_2 (determined by measurement of an area of 0.20 cm^2) is applied onto the substrate using a screen-printing technique, with a 20 nm particle size paste. After applying the TiO_2 layer, the material is submitted a series of drying and heat treatments at progressively higher temperatures. After sintering, the layer is treated again with TiCl_4 and heated to 500°C for 30 min. For the preparation of counter electrodes, a 1 mm hole is drilled into an FTO plate, followed by application of the same cleaning process used for the FTO glass substrates. A $10 \mu\text{L}$ H_2PtCl_6 solution in EtOH is deposited onto the plate, and then heat-treated at 500°C for 30 min. At the time a hot-melt ionomer resin spacer is inserted between the dye-coated TiO_2 electrode and the counter electrode. Subsequent, the electrolyte solution is introduced into the cell through the drilled hole, using a vacuum backfilling method, and the hole is sealed. Light absorption is enhanced by attaching a reflective foil to the rear side of the counter electrode, directing any unabsorbed light back towards the photoanode.



Scheme 8. Schematic illustration of the structure of a dye-sensitized solar cell device ⁷⁸.

A survey of commonly used photocatalyst substances ^{124, 125} revealed that they fall into three main categories: semiconductor materials, graphene-based nanocatalysts, and organometallic complexes. The semiconductor group includes a diverse range of inorganic binary compounds, including (but not limited to) TiO₂, ZnO, CdS, and SiC. The performance of these semiconductor photocatalysts depends on a few critical factors: (1) the band gap width of the semiconductor, which determines the photon absorption spectrum for generation of electron-hole pairs; (2) efficient separation and transport of the electron-hole pairs to the surface of the material; and (3) the number and accessibility of active sites that are available for the photocatalytic reactions to occur.

DSSCs offer several advantages that make them an attractive option for solar energy conversion, including: (1) low manufacturing cost, since DSSCs can be produced at a lower cost than traditional silicon-based solar cells ¹²³; (2) absorption of fluorescent light, in addition to sunlight, which is beneficial for indoor applications ¹²³; (3) flexibility in the design and application of the solar cells, as a result of the thin-film nature of DSSCs ¹²⁶; (4) good performance under conditions of low light, making them useful in less sunny climates ¹²⁷; (5) use of eco-friendly materials in the construction of DSSCs, contributing to a greener production process ¹²⁸; (6)

versatility for use in a wide range of environments and ability to be integrated into various solar products ¹²⁸.

The unique properties of DSSCs make them an innovative solution for sustainable and adaptable energy generation. They are highly suitable for powering portable devices and are ideal for low-density power needs where conventional solar panels might be limited in terms of efficiency or cost-effectiveness. Standard roll-printing methods can facilitate the production of DSSCs, enhancing their appeal by features such as partial flexibility, translucency, and the use of economical materials.

Nonetheless, DSSCs still have some drawbacks, such as the requirement for expensive components including platinum and ruthenium, while the liquid electrolyte can cause problems that make them less durable and unable to function in all weather conditions. Despite these hurdles, DSSCs stand out as a viable and cost-effective alternative to traditional silicon-based photovoltaic cells, particularly for applications that demand flexibility and affordability.

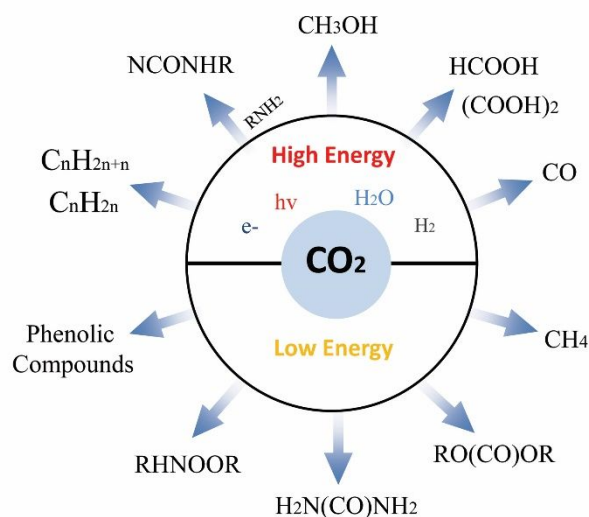
4.2. Application of DSSCs in CO₂ conversion

DSSCs have recognized potential in various applications, including the conversion of CO₂ to obtain useful products ¹²⁹. The literature lacks specific details on the application of DSSCs in CO₂ conversion, but nonetheless highlights the versatility and benefits of DSSCs for use in energy harvesting and low-carbon technologies. DSSCs can be integrated into systems that aim to reduce CO₂ levels by converting the gas into valuable chemicals or fuels by photocatalytic processes. The ability of DSSCs to effectively harness solar energy makes them suitable for powering reactions that can transform CO₂ into compounds such as formic acid, methanol, or other carbon-based products. This process not only helps in mitigating CO₂ emissions, but also provides a sustainable pathway for chemical synthesis.

This process essentially mimics photosynthesis ⁷⁸, using solar energy to convert CO₂ into organic compounds. The efficiency and selectivity of the CO₂ conversion depend on various factors, including the type of dye used, the semiconductor material, and the nature of the redox couple. Research is ongoing to optimize these aspects and improve the overall efficiency of the process. DSSCs offer a promising route for sustainable energy production and CO₂ utilization, contributing to the reduction of greenhouse gases and the generation of renewable fuels.

Improving the capability of solar cells to convert solar energy and CO_2 into high-value products such as HCOOH , CO , CH_2O , CH_3OH , and CH_4 is of paramount importance¹³⁰. The family of carboxylic acids is varied, including compounds such as formic acid, acetic acid, benzoic acid, acetylenic acid, amino acids, and lactic acid, which can be produced by different photocatalytic reaction pathways. Scheme 9 shows different chemical produces from CO_2

Any chemical transformation of CO_2 requires energy, but there are distinct processes with varying energy requirements. Low-energy processes incorporate the entire CO_2 molecule into an organic or inorganic substrate. For instance, consider the series: $\text{CO}_2 \rightarrow \text{HCOOH}$ (formic acid) $\rightarrow \text{CO} \rightarrow \text{CH}_2\text{O}$ (formaldehyde) $\rightarrow \text{CH}_3\text{OH}$ (methanol) $\rightarrow \text{CH}_4$ (methane). These reactions primarily yield products used in the chemical industry. In high-energy processes, the carbon atom's oxidation state is reduced from +4 in CO_2 to -4 in methane (CH_4). These processes have the potential to produce fuel¹³⁰. If we focus solely on chemical synthesis, we'll recycle limited amounts of CO_2 . However, if we prioritize fuel we could potentially recycle larger volumes of CO_2 . The ongoing processes developments relevant to the chemical industry, and reactions pertinent to the energy sector. Ultimately, finding sustainable energy solutions will be a key to unlocking the full potential of CO_2 conversion¹³⁰.



Scheme 9. Production of chemicals from CO_2 at different energy level.

However, the large-scale synthesis of carboxylic acids faces challenges, especially when it involves the conversion of lignocellulosic biomass, which requires hydrolysis and electrophilic attack by metal-organic reagents. These processes often have drawbacks such as high energy consumption, low efficiency, and poor product selectivity ^{134, 135}. To address these issues, the adoption of green and efficient methods is crucial for the production of diverse carboxylic acids by CO₂ reduction. Carboxylic acids are attractive products, with high commercial value and advantages including low toxicity, high energy density, and greater energy value per kilowatt-hour, compared to other products. These acids are utilized in a wide range of industries, from rubber production to the manufacture of flavorings, cosmetics, pharmaceuticals, and pesticides.

4.3. Mechanism of CO₂ conversion in DSSCs

In DSSCs, the conversion of CO₂ is facilitated by a photoelectrochemical process, with the DSSC acting as a catalyst for the transformation of CO₂ into useful substances. Sunlight is captured by the dye sensitizer, which then energizes the electrons of the dye. These energized electrons are propelled into the conduction band of the semiconductor (typically TiO₂), which constitutes the anode. The electrons then traverse the external circuit and reach the cathode, where they participate in reduction reactions. At this stage, the electrons convert CO₂ into a variety of carbon-based compounds, such as hydrocarbons or alcohols. Concurrently, the dye molecules, now oxidized, are regenerated by acquiring electrons from the redox couple of the electrolyte solution. Electrons flowing from the cathode replenish the redox couple, closing the electrical loop ¹²³.

Enhancing the efficiency of solar cells is crucial for optimizing the conversion of solar energy and CO₂ into valuable products such as HCOOH, CO, CH₂O, CH₃OH, and CH₄ ¹³⁰. Among these products, carboxylic acids, especially formic acid (HCOOH) ¹³³, are of particular interest, due to their commercial significance and attractive characteristics including low toxicity, high energy density, and greater energy value per kWh, compared to other products. The versatility of formic acid enables its use in many industrial applications, including those mentioned above.

Carboxylic acids encompass a diverse array of compounds, including formic acid, acetic acid, benzoic acid, acetylenic acid, amino acid, and lactic acid. In photocatalytic processes, these acids can be synthesized according to various pathways (see Scheme 10). However, the industrial

production of carboxylic acids has been hindered by the fact that methods involving the breaking down of lignocellulosic biomass by hydrolysis and electrophilic attack with metal-organic reagents have high energy costs, low efficiency, and poor product selectivity^{131, 132}. To address these issues, there is an urgent need for sustainable and effective techniques to generate a range of carboxylic acids by CO₂ reduction. Honda et al. accomplished the photocatalytic reduction of CO₂ to hydrocarbons in 1970¹³⁴. Subsequent research has continued to advance the field of photocatalytic CO₂ reduction¹³⁵⁻¹³⁷.

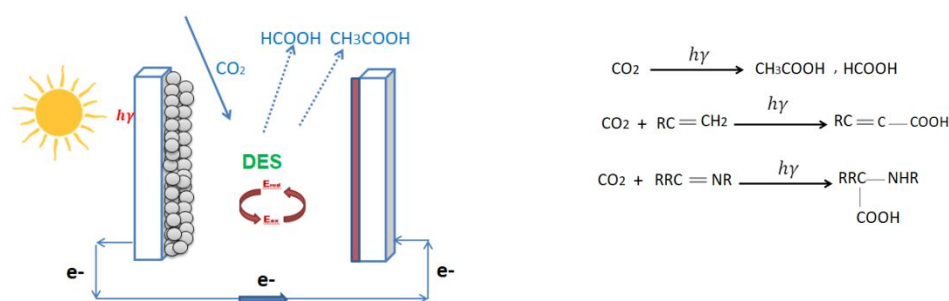
Green methods for producing carboxylic acids offer several significant benefits: (1) they are environmentally sustainable, since these methods typically avoid the use of heavy metals and strong acids, reducing the environmental impact; (2) green techniques often require less energy, contributing to lower production costs and a smaller carbon footprint; (3) cost-effectiveness is improved by the absence of byproducts and the ability to recover and recycle solvents; (4) harmful emissions are reduced in processes that do not generate nitrogen oxides (NO_x) or other greenhouse gases that have climate implications; (5) the use of renewable feedstocks contributes to the long-term sustainable production of carboxylic acids. These advantages align with the global shift towards more sustainable and eco-friendly industrial processes¹³⁸.

The process of converting CO₂ into carboxylic acids by photocatalysis, shown in Scheme 10, begins when the catalysts, typically semiconductor materials, are subjected to light irradiation. This exposure causes electrons within the semiconductor to become excited, leaving behind positively charged vacancies known as holes. These photogenerated electron-hole pairs are crucial to the process, as they are separated and directed towards the active sites of the catalyst.

Once at the surface, the photogenerated electrons assist in the reduction of CO₂, transforming it into various useful fuels (CO, CH₄, CH₃OH, and others). The presence of water (H₂O) can influence the reaction, but is not always necessary. The number of electrons participating in the chemical reaction determines the specific products formed during this process. For instance, the formation of CO or formic acid (HCOOH) requires two electrons (2e⁻), while the production of methanol (CH₃OH) necessitates six electrons (6e⁻), and methane (CH₄) production requires eight electrons (8e⁻)^{139, 140}.

This photo-electrocatalytic process is a promising green technology for CO₂ reduction, as it utilizes sunlight, a renewable energy source, and can potentially lead to the creation of valuable chemicals and fuels. The efficiency and selectivity of the process can be influenced by the choice

of semiconductor material, the design of the catalyst, and the reaction conditions. Studies continue to explore and optimize these factors to enhance the conversion rates and the yields of desired products ¹⁴¹.



Scheme 10. Different carboxylic acid reaction paths in solar cells ¹³⁰.

4.4. DESs as electrolytes in DSSCs

Deep eutectic solvents (DESs) are used as electrolytes in solar cells due to several compelling benefits. DESs are biodegradable and nontoxic, making them environmentally friendly, as well as cost-effective and able to enhance certain performance metrics of solar cells, such as the open-circuit voltage (V_{oc}) and the short-circuit current (I_{sc}), depending on their

molecular structure. They are inexpensive to produce and can be prepared on a large scale, which is advantageous for commercialization. Furthermore, they are stable and can contribute to the long-term stability of solar cells, which is crucial for practical applications. In addition, DESs can dissolve a wide range of substances and their physicochemical properties can be tuned by including different hydrophilic or hydrophobic components. These properties make DESs suitable for use in DSSCs and other photovoltaic devices, aligning with the goals of producing low-cost and eco-friendly materials for large-scale production^{60, 141}.

As discussed above, DSSCs consist of an anode made of a thin titanium dioxide (TiO_2) layer that is sensitized by a suitable dye^{142, 143}. A cathode containing Pt nanoparticles and a liquid electrolyte solution with a redox couple facilitate dye regeneration and complete the electrical circuit. The affinity of the dye for water (hydrophilicity) or its repulsion of water (hydrophobicity), as well as the choice of metal for dye optimization, are critical factors in enhancing the efficiency of photochemical cells and have been the subject of extensive research^{25, 144, 145}. Volatile organic compounds (VOCs), such as acetonitrile or nitriles, are commonly used as solvents in electrolyte solutions for DSSCs. However, drawbacks of VOCs include flammability, volatility, and possible toxicity. This can hinder the wider adoption of DSSCs as environmentally sustainable sources of renewable energy.

In the DSSC, the dye molecule becomes excited when exposed to light, transferring an electron to the TiO_2 and a hole to the redox couple, for the process to work. This process resets the dye to its original state, allowing the device to continue functioning and prepare for the next cycle. The I^-/I_3^- redox couple is the one most used in DSSCs, although other redox couples such as $\text{CO}_2^{2+}/\text{CO}_3^{3+}$ or $\text{Cu}^+/\text{Cu}^{2+}$ have also been explored for their potential benefits^{146, 147}.

4.5. Efficiency of DSSCs (J/V curve)

The efficiency of DSSCs is often represented by the J/V curve, which is a plot of the current density (J) vs. the voltage (V), under illumination. The J/V curve measurement is a crucial technique for characterizing solar cells, involving determination of the current density (J) generated by the cell as the applied voltage (V) is varied, under a solar light source. This curve, obtained under illumination, enables determination of all the key parameters of a photovoltaic (PV)

device, such as the power conversion efficiency (PCE) as a very important factor, the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}), and the fill factor (FF). The J_{sc} value represents the peak current output of the cell, observed at zero voltage, while the V_{oc} represents the highest voltage achievable, measured when the current output is zero. FF is a measure of the power output efficiency of the cell, calculated as the ratio of the actual power output (P_{out}) to the theoretical maximum power ($J_{sc} \times V_{oc}$). PCE is defined as the ratio of the power output (P_{out}) to the power input (P_{in}), with the output power density being the product of J_{sc} , V_{oc} , and FF. Therefore, PCE can be expressed by the following equation:

$$(\eta) \text{ PEC} = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad (1)$$

Several strategies can be used to improve the efficiency of DSSCs, such as optimizing the dye molecules, using dyes with broader light absorption spectra (including the visible and near-infrared ranges) to capture more sunlight, improving the redox mediator, or using solid-state hole transport materials (HTMs) for better charge transport and reduced recombination. Improvement of photoanodes can be achieved using nanostructured materials (such as TiO_2) to increase the surface area available for dye adsorption and light harvesting. Counter electrodes composed of alternative carbon-based or platinum materials can present enhanced catalytic activity and stability. By focusing on these areas, studies aim to extend the limits of DSSC performance, making them more competitive with traditional silicon-based solar cells ^{78, 148, 149}.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the sensitizer play a pivotal role in DSSCs, and understanding the interplay between HOMO/LUMO levels, charge distribution, and the sensitizer's mechanism is essential for designing efficient DSSCs to offer promise for clean, renewable energy production and contribute to sustainable development. The HOMO represents the energy level of the highest electron that can be excited, while the LUMO represents the lowest energy level of an unoccupied electron. The sensitizer enables electron injection into the semiconductor. Efficient sensitizers have a small energy gap between their HOMO and LUMO levels. The small distance between the two entities results in enhanced charge separation during the process of photo excitation ¹⁵⁰. Sensitizers are

crucial because they absorb sunlight and generate excited electrons. They must have appropriate HOMO and LUMO levels to match the redox potentials of the semiconductor and the electrolyte. Sensitizers can be organic (metal-free) or inorganic (such as ruthenium-based dyes). Organic sensitizers are chosen because they are not toxic, readily available, and cost-effective ¹⁵¹.

Theoretical studies, especially using Density Function Theory (DFT), provide valuable insights for advancing solar cell technology by considering HOMO/LUMO levels, charge distribution, and the sensitizer's mechanisms. In the charge distribution mechanism, when sunlight hits the DSSC, the sensitizer (usually an organic dye) absorbs photons and gets excited. The excited sensitizer transfers an electron from its HOMO to its LUMO level. This electron then moves to the semiconductor (often titanium dioxide, TiO₂) through the electrolyte. The difference in chemical potential between the electrolyte and the semiconductor drives this charge transfer.

Researchers employ DFT to investigate the electronic structure and properties of sensitizers. DFT calculations show that HOMO and LUMO are spread out in space at the interface. This helps excitation break apart and lines up the energy levels in a way that is good for charge transport. An investigation was conducted on graphene-based sensitizers using Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TD-DFT) in order to comprehend their influence on photophysical properties¹⁵⁰. Additional research investigates potential sensitizers for DSSC, such as nanocomposites of graphene quantum dot hybrids and their Cu-metallated macrocycles ¹⁵¹. Besides, other study examined the structural and electrical characteristics, as well as the absorption spectra, of supramolecular triads consisting of fullerene and porphyrine in DSSCs¹⁵². The HOMO and LUMO states of the C60-P-Mp triad are primarily located on the Mp unit, with the C60 cage unit acting as the donor and the C60 fullerene unit acting as the acceptor. This pattern is observed in the C60-P-ZnPDouble complex, C60-P-FeP, and C60-P-ZnP complexes. When the position of porphyrine and ZnP changes, the HOMO density is mostly on the C60 fullerene and linkage groups. On the other hand, the LUMO density is mostly in the porphyrine moiety ¹⁵².

Optimizing the band gap, maximizing JSC, and achieving an appropriate Voc are essential for enhancing the overall performance of DSSCs. Researchers continually explore new materials and sensitizers to improve these parameters and make solar energy conversion more efficient ¹⁵²,

¹⁵³. There is a difference in energy between the molecular orbitals that are most full (HOMO) and least full (LUMO) in the semiconductor material, which is usually titanium dioxide (TiO₂). This is called the band gap (E_g). A smaller band gap allows the semiconductor to absorb a broader range of photons from sunlight.

As explained, when a photon with energy greater than the band gap is absorbed, an electron is excited from the valence band (HOMO) to the conduction band (LUMO). The band gap influences the efficiency of charge separation and electron injection into the semiconductor. Short-Circuit Current Density (J_{SC}) represents the maximum current density generated by the DSSC under short-circuit conditions (i.e., when no external load is connected), and it depends on the following factors: a) photon absorption: A larger band gap results in a lower J_{SC} because fewer photons are absorbed. B) sensitizer efficiency: c) efficient sensitizers absorb more photons, generate more excited electrons, and f) charge transport: More electrons moving from the sensitizer to the semiconductor is what causes higher J_{SC}. This is directly related to the amount of photons absorbed and how well charges are transferred. Furthermore, open-circuit voltage (V_{oc}) is the voltage across the DSSC terminals when no current flows (i.e., under open-circuit conditions), and it is dependent upon the following factors: a) recombination losses: b) reducing charge recombination improves V_{oc}, which is directly related to the energy alignment between the sensitizer and the redox couple; c) energy levels: d) the difference between the sensitizer's HOMO/LUMO levels and the electrolyte's redox potential; and e) electron injection efficiency: Higher V_{oc} is the result of efficient electron injection ¹⁵².

The Light Harvesting Efficiency (LHE) of DSSCs is a key factor in their performance. LHE measures the efficiency of a DSSC in capturing and converting incoming solar energy into useful electrical energy. It denotes the proportion of photons that are absorbed and contribute to the production of photocurrent ¹⁵³. A higher LHE results in improved utilization of sunshine, which in turn leads to an improvement in power conversion efficiency (PCE). Effective light harvesting maximizes the utilization of the sensitizer's absorption spectrum. The sensitizer of choice determines the absorption spectrum. Sensitizers with a wide range of absorption spectra improve LHE. It is very important that electrons move efficiently from the

excited sensitizer to the semiconductor material, like TiO_2 . Maximizing LHE involves minimizing charge recombination and enhancing light trapping within the DSSCs¹⁵². In order to enhance LHE, it is necessary to fine-tune the sensitizing properties, developing sensitizers with ideal HOMO-LUMO energy levels and absorption characteristics¹⁵³. In addition, the integration of nanostructures such as nanowires and nanoparticles can be employed to improve the capture and absorption of light¹⁵⁴. Light harvesting can be made even more effective by using different sensitizers that have absorption spectra that work well with each other and by making the path length of photons longer inside the cell¹⁵⁵.

The calculated LHE for triad complexes using ZINDO/S method reported¹⁵², the highest value of oscillator strength (13.8) is related to the C60-P-NiP in 545.1 nm wavelengths while lowest value (0.46) belongs to the C60-P-TiP in 478.5 nm.

The study on the same evaluation for Zn complexes¹⁵² revealed that the oscillator strength value for C60-P-ZnP (5.20) is higher than C70-P-ZnP (3.95), when the position of porphyrine and ZnP changed in C60-P-ZnP complex and the LHE and oscillator strength was enhanced. The same trend is observed in doubly C60-P-ZnP complex. In this case the oscillator strength value is 8.20, and consequently the LHE increase sharply. In conclusion, the LHE was improved by increasing the conjugation, and it is exhibited that doubly complex with longer π conjugations showed oscillator strength and light harvesting efficiency, thus leading to higher triad efficiency, and stability. Similar estimation has also been carried out for the same triad and reported^{152, 156}.

ILs/DESs have been used as electrolytes in DSSCs since 2009¹⁷, including a quaternary ammonium salt-derivative ionic liquid called G.CI, which is a eutectic mixture of glycerol (GLY) and choline iodide (CI), in a specific ratio, with 0.5 M of a mixture of N-methylbenzimidazole and 1-propyl-3-methylimidazolium iodide ([PMIM]I). The high cell performance made the G.CI DES a strong candidate for use in the future development of DSSC electrolytes.

Other studies^{157, 158} have investigated the development of novel eco-friendly DESs for use as electrolytes in DSSCs, such as DESs formulated from chlorine chloride (ChCl) and ethylamine hydrochloride (MEA.Cl) as hydrogen bond acceptors (HBAs), combined with hydrogen bond donors (HBDs) such as glycerol (Gly), ethylene glycol (EG), and imidazole (IM), in varying HBD to HBA molar ratios (1:1, 1:3, and 1:6).

The findings of the present review, considering the existing literature, indicate the need for further research to fully understand the processes involved in the use of these DESs, with a focus on the HBDs and HBAs illustrated in Table 2 summarizes the DESs used as electrolytes in DSSCs, reported in the literature.

Table 2. Overview of DSSCs using DESs as electrolytes (T = transparent layer, S = scattering layer).

DESs	Iodide source	Dye / other adsorbent	TiO ₂ thickness	Dilution	Remark	Advantages	Ref.
Choline chloride + glycerol	PMII 13:7 v/v 3 M	D149	6 µm T + 5 µm S	15% w/w water	Pioneering work that opened new possibilities for ionic liquid-based DESs in DSSCs.	Introduced a new type of DES for DSSCs, potentially enhancing electrolyte performance.	17
Aqueous choline chloride-based DESs	KI 2 M PMII 2 M	PTZ-TEG / GlcA 1:10	5 µm T 2.5 µm T	40% w/w water	Showcased the practicality of aqueous DES in real-world applications.	Demonstrated effective use of aqueous DES as an electrolyte solution in DSSCs.	16
Menthol-based hydrophobic eutectic solvent, DL-menthol /AcOH	DMII 1.0 M	PTZ-Glu / GlcA 1:10	2.5 µm T	10% v/v EtOH	Focused on sustainability and environmental friendliness.	Designed eco-sustainable DSSCs with improved electrolyte medium.	47
Sugar-based natural DESs; choline chloride-Gly, -Glu, -Sorb, -Fru, -Man	PMII 2 M	PTZ-Glu / GlcA 1:10	2.5 µm T	20% w/w water 30% w/w water 40% w/w water	Highlighted the performance benefits of using natural components.	Used eco-friendly DES for better electrolyte solutions in DSSCs, showing active role in performance increase.	159
Choline chloride + ethylene glycol (EG)	KI 0.6 M KI 0.3 M Emiml 0.3 M Emiml 0.6 M	N719	T	5% v/v water	Offered a comprehensive understanding of DES behavior in DSSCs.	Provided insights from both experiment and simulation on DES in DSSCs.	54
Canonical choline chloride-based DESs	KI 0.5 M	N719	T	30% w/w water	Assessed the benchmark DES, setting a standard for comparison.	Evaluated the performance of canonical DES as DSSC electrolytes.	50
Alkali iodide DES; LiI/EG NaI/EG KI/EG	Used in prepared DESs	N719	10 µm T + 5 µm S	No diluting agent	Investigated new DES formulations for potential improvements.	Explored alternative DES electrolytes for DSSCs.	160
Choline chloride + urea	Coupled redox mediator (e.g., I ⁻ /I ₃ ⁻)	N719	T	No diluting agent	Improved open circuit voltage (V _{oc}).	Simple preparation, biodegradable, low-cost.	60
Choline chloride + ethylene glycol	Coupled redox mediator (e.g., I ⁻ /I ₃ ⁻)	N719	T	No diluting agent	Increase in short circuit current (I _{sc}).	Nontoxic, available materials, comparative conversion efficiency.	60
Betaine + glycerol	Coupled redox mediator (e.g., I ⁻ /I ₃ ⁻)	N719	T	No diluting agent	Comparable efficiency to conventional electrolytes.	Renewable, biodegradable, non-corrosive.	60
Choline chloride + phenol	Redox mediator (e.g., I ⁻ /I ₃ ⁻)	N719	T	No diluting agent	Improved V _{oc} values by 10-40 mV, higher short circuit current (I _{sc}) not observed with 4-TBP	Eco-friendly, low cost, simple synthesis, used new efficient and eco-friendly additives.	77

The key parameters to assess in DSSC applications include the open-circuit voltage (V_{oc}), the short-circuit current density (J_{sc}), the fill factor (FF), and the overall power conversion efficiency (η). Certain DESs are emerging as promising electrolytes for DSSC applications, due to their ability to achieve higher V_{oc} values (up to 140 mV), maintain comparable FF, but exhibit lower J_{sc} , when compared to a standard electrolyte, under identical experimental conditions. The use of these DESs in DSSCs requires determination of their total energy efficiency and viability as sustainable electrolytes.

Another crucial metric is the external quantum efficiency of a DSSC, which quantifies the efficiency of conversion from incident photons to the current generated. This efficiency is known as the incident photon-to-current conversion efficiency (IPCE) and varies with the wavelength (λ). For this assessment, the photocurrent is measured under open-circuit conditions, during exposure of the cell to monochromatic light. The IPCE is calculated for each point by determining the ratio of the number of electrons harvested to the number of incident photons, at a specific wavelength (λ)^{17, 161}.

In the context of DSSCs, it is essential to consider the following aspects: robustness of the absorption coefficients and the capacity of the designed DESs to dissolve CO_2 ; significant molar extinction coefficients; and toxicity and ecological consequences. Furthermore, it is essential to undertake a thorough analysis of the physicochemical characteristics of DESs, the underlying absorption mechanisms, and the influence of the molar quantities of hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) utilized in the formulation of DESs.

In a study by Nguyen et al.¹⁸, a novel electrolyte for DSSCs was formulated by blending a choline chloride-phenol DES with acetonitrile (ACN), in varying proportions. The most favorable outcomes were obtained using an electrolyte composed of 20% DES in ACN, together with 0.03 M iodine, 0.6 M tetrabutylammonium iodide, 0.1 M guanidinium thiocyanate, and 0.5 M 4-tert-butylpyridine. This specific composition was instrumental in enhancing the stability and photovoltaic efficiency of the DSSCs. The improvement was attributed to the interaction of the choline and phenol components of the DES with the TiO_2 surface, which was more effective than in cells without DES.

One of the pioneering studies to demonstrate the potential of DESs as solvents in DSSCs was the work of Jhong et al.¹⁷, who employed an electrolyte solution consisting of 0.2 M iodine and 0.5 M N-methylbenzimidazole, mixed with 1-propyl-3-methylimidazolium iodide and a

choline iodide/glycerol DES. This solution was used in conjunction with the organic sensitizer D149. Building on this research, Boldrini et al.¹⁶ introduced an aqueous electrolyte based on a choline chloride-glycerol DES, which included iodine, potassium iodide, or PMII, and additional compounds such as guanidinium thiocyanate, 4-picoline, or pyridine, paired with a phenothiazine-based organic dye as the photosensitizer.

Many investigations have aimed at the development of highly efficient DSSCs. A binary solution of deep eutectic solvent (DES) with acetonitrile (ACN) showed the most promising results, among these studies^{25, 162, 163}. It was found that this mixture greatly improved the diffusion of the redox couple (I^-/I_3^-) and the electrochemical properties of the electrolyte solutions, resulting in satisfactory functioning of the device. Studies have also tested the use of additives including PMII, GuSCN, pyridine, 4-tBP, and ACN to further enhance the performance of DSSCs^{16, 18}. However, despite the promising results, potential toxicological issues and high volatility may limit the practical applications of these additives. Therefore, there is a need for safer and more efficient alternatives for large-scale practical applications. Continued research is necessary to identify and develop new additives that can improve the performance of DSSCs, without compromising safety or practicality. With further advancements in this field, DSSCs have the potential to become a highly efficient and sustainable source of renewable energy.

To better understand the movement of electron carriers in electrolyte solutions and their interactions with solvents and surfaces, molecular dynamics (MD) simulations have been utilized in conjunction with experimental methods to investigate the effects of electrolytes on DSSC efficiency¹⁶⁴⁻¹⁶⁶.

One area of focus was the behavior of DES composed of choline chloride and ethylene glycol (ChCl-EG), at a 1:2 molar ratio, as solvent in DSSC electrolytes. The aim was to examine the photovoltaic properties of a DES-based electrolyte for DSSCs. The ChCl-EG DES was chosen due to its relatively high ionic conductivity of 7.61 mS cm^{-1} at 298 K, attributed to its lower viscosity than other DESs that have been studied. Elsewhere, a 40% water content of a DES consisting of choline chloride and glycerol (ChCl/Gly, 1:2 mol/mol) was reported to provide an effective electrolyte solvent for DSSCs¹⁶. This study found that the best DSSC performance was obtained using a 2 M concentration of 1-propyl-3-methylimidazolium iodide ([PMIM]I) and 0.1 M of guanidinium thiocyanate (GuSCN) in a 40% aqueous solution of ChCl:Gly, resulting in a

power conversion efficiency (PCE) of 1.7%. Further research is necessary to explore the potential of DESs with other additives for improving DSSC performance in a safe and practical manner.

A recent study ¹⁶¹ investigated the use of different alkali metal iodide-based deep eutectic solvents (DESs) as electrolytes for DSSCs. These DESs included LiI:nEG, NaI:nEG, and KI:nEG, with varying amounts of iodine added to improve their performance. The results showed that the open-circuit voltage (V_{oc}) under illumination increased with increasing cation radius from Li^+ to K^+ . When compared to a reference electrolyte in the same experiment, the DESs had higher V_{oc} (up to 140 mV), similar fill factor values, but lower current density values. After optimization, the DES electrolytes could be used in DSSCs as a promising alternative to electrolytes based on volatile organic compounds. A mixture of choline chloride (ChCl, 1 mol) and ethylene glycol (EG, 2 mol) in combination with lithium iodide (LiI), 1-ethyl-3-methylimidazolium iodide (EMIM), MeCN, and iodine was used to develop a cost-effective and sustainable DES-based electrolyte solution for DSSCs with TiO_2 and Pt electrodes. Different iodine amounts were added to the original DES electrolyte to improve its electrolytic performance. On illumination, V_{oc} increased with increase of the cation radius from Li^+ to K^+ . When compared to a reference electrolyte, under the same experimental conditions, these DESs presented higher V_{oc} values (up to 140 mV) and similar FF values. However, they had lower current density values. Improvement of these DES electrolytes could enable their use in DSSCs as a viable alternative to VOC-based electrolytes. Subsequently, a cost-effective and sustainable DES electrolyte was successfully developed, consisting of a mixture of choline chloride (ChCl, 1 mol) and ethylene glycol (EG, 2 mol) in combination with lithium iodide, 1-ethyl-3-methylimidazolium iodide (EMIM), MeCN, and iodine, for use in a DSSC with TiO_2 and Pt electrodes ¹⁶¹.

4.6. Challenges, opportunities and future directions

The utilization of DESs in environmentally-friendly DSSCs presents both opportunities and challenges, such as: (1) traditional liquid electrolytes have drawbacks such as volatility and environmental hazards; on the other hand, DESs electrolytes face viscosity issues, and high viscosity in DES can hinder ionic diffusion of redox mediators, affecting conversion efficiency. (2) Finding suitable DES-based electrolytes remains a challenge for large-scale DSC production. (3) DES stability at elevated temperatures is crucial to study to prevent thermal degradation of

components. (4) Knowing when DES changes phases (solid, liquid, or gel) is important for getting the most out of their use in DSSCs. The density and viscosity of DES affect how they flow inside the solar cell. High ionic conductivity is desirable for efficient charge transfer. (5) The properties of surface tension and polarity influence DES wetting behavior on the TiO_2 -loaded dye-sensitized photoanode. The advantages included: (1) they can be synthesized from inexpensive, nontoxic starting materials, making them eco-friendly and offering a low-cost alternative to conventional ionic liquids. (2) DES-based solar cell devices exhibit competitive conversion efficiency compared to popular ionic liquids, which increase the efficiency of the cells. Because of the advantages of utilizing deep eutectic solvents (DES) in environmentally friendly DSSCs, researchers continue to explore DES properties and address challenges to enhance their performance^{167, 168}.

Addressing the mentioned challenges requires a combination of experimental investigations, computational modeling, and innovative thinking. Possible strategies that could be used to address these challenges are as follows: (1) Mixing DESs with ionic liquids with low viscosity or adding items (like salts or co-solvents) to make them less viscous or less conductive and more stable at high temperatures. (2) Selecting suitable HBDs and HBAs (e.g., choline chloride, urea) to achieve optimal ionic conductivity and viscosity and improved thermal stability by altering hydrogen bond interactions or introducing functional groups. (3) Using nanostructured materials (e.g., mesoporous TiO_2) to accommodate DES phase changes. (4) Applying thin coatings (e.g., graphene, polymers) to improve DES adhesion and stability. (5) Modifying TiO_2 electrodes with hydrophilic or DES-compatible functional groups to enhance wetting behavior. (5) Optimizing ion migration pathways within the cell to minimize DES viscosity effects. (6) Investigating DES recyclability and exploring methods for reusing or regenerating DES. (7) Engaging industry partners to bridge the gap between fundamental research and practical applications of DESs.

The perspectives related to the use of DESs in DSSCs can be described as follows: (1) Combining DES with polymers to create hybrid materials. These blends could offer improved mechanical strength, thermal stability, and ion transport properties, or combine graphene into DES to enhance electrical conductivity and provide a conductive network within the electrolyte. (2) Developing DES that responds to environmental cues (e.g., temperature, light) by altering its properties. This adaptability could enhance DSSCs performance under varying conditions. (3) Investigating DES for super-capacitor applications. Their unique properties may lead to high-capacity, environmentally friendly energy storage devices. (4) Utilizing DESs as thermoelectric materials for converting sun heat and CO₂ into added-value products (5) Developing efficient methods to recycle DES after their useful life in DSSCs and promoting DES-based technologies beyond solar cells, such as in sustainable chemical processes or green manufacturing.

The present review summarizes the use of various eutectic mixtures as strong electrolytes in DSSCs, considering the different factors affecting the performance of these solar cells. Deep eutectic solvents (DESs) are more viscous than volatile organic compound (VOC) electrolytes, but they have been shown to greatly improve cell efficiency in thin-film DES-DSSCs by raising the photovoltage. DESs could make a major contribution to the development of long-lasting and environmentally-friendly liquid DSSCs, due to their advantages in terms of performance metrics, providing higher voltage and lower recombination resistance. This would support a shift towards a more environmentally aware approach to industrial progress.

5. Conclusions

Solar devices based on deep eutectic solvents (DESs) are at the forefront of sustainable and environmentally friendly green technologies. These innovative systems have the potential to significantly enhance the availability of clean and renewable energy sources within both the scientific realm and the broader societal context over the coming years. However, this potential can only be achieved by a dedicated investment in fundamental research. A comprehensive understanding of the intricate role played by DESs is crucial, especially concerning their intermolecular interactions involving the diverse components of solar cell structures. Such knowledge is essential for harnessing their positive impact on charge transfer processes at the molecular level. The application of DESs across diverse scientific disciplines is an emerging and exciting area of technology, with great potential for large-scale industrial application. Contrary to initial assumptions, on an industrial level, the transformation of two solid substances into a liquid form presents certain complexities. DESs are highly adaptable mixtures, comprising a variety of hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs). Consequently, for the transition of DESs into a tangible industrial entity, researchers have been concentrating on developing a variety of scalable preparation techniques.

As discussed in this review, the physicochemical properties of DESs have a major impact on their performance as electrolytes in dye-sensitized solar cells (DSSCs). DESs are known for their low volatility, strong solubilization capacity, and excellent ionic conductivity, which are crucial for the efficient operation of DSSCs. Their tunable nature allows the optimization of these properties to enhance the charge transport and stability of solar cells. In addition, the ability to tailor DESs by adjusting the HBA/HBD ratio provides a pathway for fine-tuning the polarity and viscosity of the solvent, further improving DSSC performance. In brief, the unique physicochemical properties of DESs offer a promising avenue for the development of high-efficiency and stable DSSCs, making them a valuable component in the advancement of renewable energy technologies.

This review highlights the increasing allure of DESs as key elements in DSSCs. Recently, researchers have evaluated numerous DESs as electrolyte solvents for DSSCs, alongside other high-voltage open-circuit electrolyte components. DESs have been used as solvents with or without added water, as well as in conjunction with ionic liquids (ILs) or VOCs. A notable feature that can be seen from the existing studies is the overall enhancement in the long-term stability of

solar devices, even when DESs constitute a small fraction of the electrolyte solution. Although the efficiencies reported for DES-only DSSCs have not been as high as expected, the burgeoning interest and continuous performance advancements suggest that superior efficiencies may soon be achievable. However, using DESs in mixtures with conventional solvents to achieve higher efficiencies introduces additional VOC-related concerns, including flammability, toxicity, and volatility.

A thorough review of the literatures showed that the ability of CO₂ to dissolve in DESs can greatly improve the capacity of solar cells to convert CO₂ into useful products. In the synthesis of DESs, amine-based DESs have emerged as an excellent option for selecting hydrogen bond donors (HBDs), with their corresponding salts as hydrogen bond acceptors (HBAs). In addition, researchers have recognized ethylene glycol as an effective HBD that increases the viscosity of DESs and enhances CO₂ solubility. The addition of potassium iodide (KI) to DES formulations can further improve the performance of DSSCs.

This review highlights that the addition of water can alter the molecular structure and dynamics of DESs, consequently affecting solar cell performance and efficiency. Also uncovered is the significance of CO₂ solubility in DESs for the capture and utilization of CO₂ by solar cells. Certain DESs demonstrate a high capacity and selectivity for CO₂ absorption, while the presence of water can further enhance the absorption kinetics and capacity. Amine-based DESs are shown to be eco-friendly solvents suitable for use as electrolytes in various solar cell applications. These DESs have the potential to reach or exceed the power conversion efficiency, specific capacitance, and voltage of traditional solvents. However, it is important to acknowledge the drawbacks of DESs, such as their potential corrosiveness and the energy required for their production and use. These factors must be considered when evaluating the overall sustainability of DES-based technologies.

To conclude, the design of a specific eutectic mixture for a particular application requires a more comprehensive understanding than has so far been achieved. At the fundamental level, it is important to elucidate the structure and dynamics of DESs, considering the intermolecular interactions, the networks of bonds within HBDs and HBAs, and the roles that they play. In this way, it will soon be possible to design DESs with optimal chemical and physical characteristics for maximizing the performance of fully eco-friendly and sustainable solar devices.

CRedit author contributions

Khatereh A. Pishro: Formal analysis, Investigation, Writing- review & editing, Original draft.

Mario Henrique Gonzalez: Supervision, Conceptualization, Project administration, Resources, Writing - review & editing.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors are grateful for the financial support provided by the São Paulo Research Foundation (FAPESP, grant numbers #2015/08893-4, #2017/18531-3, #2019/22113-8, and #2021/14759-5) and the National Institute for Alternative Technologies of Detection, Toxicological Evaluation and Removal of Micropollutants and Radioactives (INCT-DATREM) (FAPESP, grant number #2014/50945-4; CNPq, grant number #465571/2014-0).

References

- (1) Armaroli, N.; Balzani, V. Solar electricity and solar fuels: status and perspectives in the context of the energy transition. *Chemistry—A European Journal* 2016, 22 (1), 32-57.
- (2) Su'ait, M. S.; Rahman, M. Y. A.; Ahmad, A. Review on polymer electrolyte in dye-sensitized solar cells (DSSCs). *Solar Energy* 2015, 115, 452-470.
- (3) Yamasaki, A. An overview of CO₂ mitigation options for global warming—emphasizing CO₂ sequestration options. *Journal of chemical engineering of Japan* 2003, 36 (4), 361-375.
- (4) Roy, S. C.; Varghese, O. K.; Paulose, M.; Grimes, C. A. Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons. *ACS Nano* 2010, 4 (3), 1259-1278. DOI: 10.1021/nn9015423.
- (5) Pye, S.; Li, F. G. N.; Price, J.; Fais, B. Achieving net-zero emissions through the reframing of UK national targets in the post-Paris Agreement era. *Nature Energy* 2017, 2 (3), 17024. DOI: 10.1038/nenergy.2017.24.

- (6) Schreier, M.; Héroguel, F.; Steier, L.; Ahmad, S.; Luterbacher, J. S.; Mayer, M. T.; Luo, J.; Grätzel, M. Solar conversion of CO₂ to CO using Earth-abundant electrocatalysts prepared by atomic layer modification of CuO. *Nature Energy* 2017, 2 (7), 1-9.
- (7) Schreier, M.; Curvat, L.; Giordano, F.; Steier, L.; Abate, A.; Zakeeruddin, S. M.; Luo, J.; Mayer, M. T.; Grätzel, M. Efficient photosynthesis of carbon monoxide from CO₂ using perovskite photovoltaics. *Nature communications* 2015, 6 (1), 7326.
- (8) White, J. L.; Herb, J. T.; Kaczur, J. J.; Majsztrik, P. W.; Bocarsly, A. B. Photons to formate: Efficient electrochemical solar energy conversion via reduction of carbon dioxide. *Journal of CO₂ Utilization* 2014, 7, 1-5.
- (9) Correa-Baena, J.-P.; Abate, A.; Saliba, M.; Tress, W.; Jacobsson, T. J.; Grätzel, M.; Hagfeldt, A. The rapid evolution of highly efficient perovskite solar cells. *Energy & Environmental Science* 2017, 10 (3), 710-727.
- (10) Gabardo, C. M.; Seifitokaldani, A.; Edwards, J. P.; Dinh, C.-T.; Burdyny, T.; Kibria, M. G.; O'Brien, C. P.; Sargent, E. H.; Sinton, D. Combined high alkalinity and pressurization enable efficient CO₂ electroreduction to CO. *Energy & Environmental Science* 2018, 11 (9), 2531-2539.
- (11) Miao, W.; Chan, T. H. Ionic-liquid-supported synthesis: A novel liquid-phase strategy for organic synthesis. *Accounts of chemical research* 2006, 39 (12), 897-908.
- (12) Budzianowski, W. M. *Energy Efficient Solvents for CO₂ Capture by Gas-Liquid Absorption: Compounds, Blends and Advanced Solvent Systems*; Springer, 2016.
- (13) Loow, Y.-L.; Wu, T. Y.; Yang, G. H.; Ang, L. Y.; New, E. K.; Siow, L. F.; Jahim, J. M.; Mohammad, A. W.; Teoh, W. H. Deep eutectic solvent and inorganic salt pretreatment of lignocellulosic biomass for improving xylose recovery. *Bioresource technology* 2018, 249, 818-825.
- (14) Ventura, S. P.; e Silva, F. A.; Quental, M. V.; Mondal, D.; Freire, M. G.; Coutinho, J. A. Ionic-liquid-mediated extraction and separation processes for bioactive compounds: past, present, and future trends. *Chemical Reviews* 2017, 117 (10), 6984-7052.
- (15) Sharma, A.; Sharma, R.; Thakur, R. C.; Singh, L. An overview of deep eutectic solvents: Alternative for organic electrolytes, aqueous systems & ionic liquids for electrochemical energy storage. *Journal of Energy Chemistry* 2023, 82, 592-626. DOI: <https://doi.org/10.1016/j.jechem.2023.03.039>.
- (16) Boldrini, C. L.; Manfredi, N.; Perna, F. M.; Trifiletti, V.; Capriati, V.; Abboto, A. Dye-Sensitized Solar Cells that use an Aqueous Choline Chloride-Based Deep Eutectic Solvent as Effective Electrolyte Solution. *Energy Technology* 2017, 5 (2), 345-353. DOI: <https://doi.org/10.1002/ente.201600420> (accessed 2023/08/25).
- (17) Jhong, H.-R.; Wong, D. S.-H.; Wan, C.-C.; Wang, Y.-Y.; Wei, T.-C. A novel deep eutectic solvent-based ionic liquid used as electrolyte for dye-sensitized solar cells. *Electrochemistry Communications* 2009, 11 (1), 209-211. DOI: <https://doi.org/10.1016/j.elecom.2008.11.001>.

- (18) to improve stability performance in dye-sensitized solar cells. *Journal of Molecular Liquids* 2019, 277, 157-162.
- (19) Florindo, C.; Lima, F.; Ribeiro, B. D.; Marrucho, I. M. Deep eutectic solvents: overcoming 21st century challenges. *Current Opinion in Green and Sustainable Chemistry* 2019, 18, 31-36.
- (20) Kim, J. Y.; Lee, J.-W.; Jung, H. S.; Shin, H.; Park, N.-G. High-efficiency perovskite solar cells. *Chemical reviews* 2020, 120 (15), 7867-7918.
- (21) Li, H.; Zhang, W. Perovskite tandem solar cells: from fundamentals to commercial deployment. *Chemical Reviews* 2020, 120 (18), 9835-9950.
- (22) Li, R.; Li, C.; Liu, M.; Vivo, P.; Zheng, M.; Dai, Z.; Zhan, J.; He, B.; Li, H.; Yang, W. Hydrogen-bonded dopant-free hole transport material enables efficient and stable inverted perovskite solar cells. *CCS Chemistry* 2022, 4 (9), 3084-3094.
- (23) Li, R.; Liu, M.; Matta, S. K.; Hiltunen, A.; Deng, Z.; Wang, C.; Dai, Z.; Russo, S. P.; Vivo, P.; Zhang, H. Sulfonated Dopant-Free Hole-Transport Material Promotes Interfacial Charge Transfer Dynamics for Highly Stable Perovskite Solar Cells. *Advanced Sustainable Systems* 2021, 5 (12), 2100244.
- (24) Ho-Baillie, A. W.; Zheng, J.; Mahmud, M. A.; Ma, F.-J.; McKenzie, D. R.; Green, M. A. Recent progress and future prospects of perovskite tandem solar cells. *Applied Physics Reviews* 2021, 8 (4).
- (25) Kakiage, K.; Aoyama, Y.; Yano, T.; Oya, K.; Fujisawa, J.-i.; Hanaya, M. Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes. *Chemical communications* 2015, 51 (88), 15894-15897.
- (26) Salvador, G. P.; Pugliese, D.; Bella, F.; Chiappone, A.; Sacco, A.; Bianco, S.; Quaglio, M. New insights in long-term photovoltaic performance characterization of cellulose-based gel electrolytes for stable dye-sensitized solar cells. *Electrochimica Acta* 2014, 146, 44-51.
- (27) Boldrini, C. L.; Manfredi, N.; Perna, F. M.; Trifiletti, V.; Capriati, V.; Abboto, A. Dye-sensitized solar cells that use an aqueous choline chloride-based deep eutectic solvent as effective electrolyte solution. *Energy Technology* 2017, 5 (2), 345-353.
- (28) Wagle, D. V.; Zhao, H.; Baker, G. A. Deep eutectic solvents: sustainable media for nanoscale and functional materials. *Accounts of chemical research* 2014, 47 (8), 2299-2308.
- (29) Choudhury, S.; Mahanta, U.; Prasanna Venkatesh, R.; Banerjee, T. Ionic liquid derived novel deep eutectic solvents as low viscous electrolytes for energy storage. *Journal of Molecular Liquids* 2022, 366, 120245. DOI: <https://doi.org/10.1016/j.molliq.2022.120245>.
- (30) Kargul, J.; Kiliszek, M. Artificial Photosynthesis. In *Bioelectrochemical Interface Engineering*, 2019; pp 271-309.

- (31) Prajapati, A.; Singh, M. R. Assessment of Artificial Photosynthetic Systems for Integrated Carbon Capture and Conversion. *ACS Sustainable Chemistry & Engineering* **2019**, 7 (6), 5993-6003. DOI: 10.1021/acssuschemeng.8b04969.
- (32) Clarke, C. J.; Tu, W.-C.; Levers, O.; Bröhl, A.; Hallett, J. P. Green and Sustainable Solvents in Chemical Processes. *Chemical Reviews* **2018**, 118 (2), 747-800. DOI: 10.1021/acs.chemrev.7b00571.
- (33) Lipshutz, B. H.; Gallou, F.; Handa, S. Evolution of Solvents in Organic Chemistry. *ACS Sustainable Chemistry & Engineering* **2016**, 4 (11), 5838-5849. DOI: 10.1021/acssuschemeng.6b01810.
- (34) Mallakpour, S.; Dinari, M. Ionic Liquids as Green Solvents: Progress and Prospects. In *Green Solvents II: Properties and Applications of Ionic Liquids*, Mohammad, A., Inamuddin, D. Eds.; Springer Netherlands, 2012; pp 1-32.
- (35) Alonso, D. A.; Baeza, A.; Chinchilla, R.; Guillena, G.; Pastor, I. M.; Ramón, D. J. Deep eutectic solvents: the organic reaction medium of the century. *European Journal of Organic Chemistry* **2016**, 2016 (4), 612-632.
- (36) Perna, F. M.; Vitale, P.; Capriati, V. Deep eutectic solvents and their applications as green solvents. *Current Opinion in Green and Sustainable Chemistry* **2020**, 21, 27-33. DOI: <https://doi.org/10.1016/j.cogsc.2019.09.004>.
- (37) Aissaoui, T., I.M. AlNashef, U.A. Qureshi, and Y. Benguerba, Potential applications of deep eutectic solvents in natural gas sweetening for CO₂ capture. *Reviews in Chemical Engineering*, 2017. 33(6): p. 523-550.
- (38) Smith, E. L.; Abbott, A. P.; Ryder, K. S. Deep Eutectic Solvents (DESs) and Their Applications. *Chemical Reviews* **2014**, 114 (21), 11060-11082. DOI: 10.1021/cr300162p.
- (39) Hansen, B. B.; Spittle, S.; Chen, B.; Poe, D.; Zhang, Y.; Klein, J. M.; Horton, A.; Adhikari, L.; Zelovich, T.; Doherty, B. W. Deep eutectic solvents: A review of fundamentals and applications. *Chemical reviews* **2020**, 121 (3), 1232-1285.
- (40) Martins, M. A.; Pinho, S. P.; Coutinho, J. A. Insights into the nature of eutectic and deep eutectic mixtures. *Journal of Solution Chemistry* **2019**, 48, 962-982.
- (41) Liu, Y.-T.; Chen, Y.-A.; Xing, Y.-J. Synthesis and characterization of novel ternary deep eutectic solvents. *Chinese Chemical Letters* **2014**, 25 (1), 104-106.

- (42) Zhang, M., et al., Insights into the relationships between physicochemical properties, solvent performance, and applications of deep eutectic solvents. *Environmental Science and Pollution Research*, 2021. 28(27): p. 35537-35563.
- (43) Florindo, C.; Oliveira, F. S.; Rebelo, L. P. N.; Fernandes, A. M.; Marrucho, I. M. Insights into the synthesis and properties of deep eutectic solvents based on cholinium chloride and carboxylic acids. *ACS Sustainable Chemistry & Engineering* **2014**, 2 (10), 2416-2425.
- (44) van Osch, D. J.; Zubeir, L. F.; van den Bruinhorst, A.; Rocha, M. A.; Kroon, M. C. Hydrophobic deep eutectic solvents as water-immiscible extractants. *Green Chemistry* **2015**, 17 (9), 4518-4521.
- (45) Chen, M.; Edlow, A. G.; Lin, T.; Smith, N. A.; McElrath, T. F.; Lu, C. Determination of bisphenol-A levels in human amniotic fluid samples by liquid chromatography coupled with mass spectrometry. *Journal of separation science* **2011**, 34 (14), 1648-1655.
- (46) Hammond, O. S.; Bowron, D. T.; Edler, K. J. The effect of water upon deep eutectic solvent nanostructure: an unusual transition from ionic mixture to aqueous solution. *Angewandte Chemie* **2017**, 129 (33), 9914-9917.
- (47) Boldrini, C. L.; Manfredi, N.; Perna, F. M.; Capriati, V.; Abboto, A. Designing eco-sustainable dye-sensitized solar cells by the use of a menthol-based hydrophobic eutectic solvent as an effective electrolyte medium. *Chemistry—A European Journal* **2018**, 24 (67), 17656-17659.
- (48) Zhang, M.; Zhang, X.; Liu, Y.; Wu, K.; Zhu, Y.; Lu, H.; Liang, B. Insights into the relationships between physicochemical properties, solvent performance, and applications of deep eutectic solvents. *Environmental Science and Pollution Research* **2021**, 28 (27), 35537-35563. DOI: 10.1007/s11356-021-14485-2.
- (49) Meng, Q.; Chen, Y.; Xiao, Y. Y.; Sun, J.; Zhang, X.; Han, C. B.; Gao, H.; Zhang, Y.; Yan, H. Effect of temperature on the performance of perovskite solar cells. *Journal of Materials Science: Materials in Electronics* **2021**, 32 (10), 12784-12792. DOI: 10.1007/s10854-020-03029-y.
- (50) Boogaart, D. J.; Essner, J. B.; Baker, G. A. Evaluation of canonical choline chloride based deep eutectic solvents as dye-sensitized solar cell electrolytes. *The Journal of Chemical Physics* **2021**, 155 (6).

- (51) Chaabene, N.; Ngo, K.; Turmine, M.; Vivier, V. New hydrophobic deep eutectic solvent for electrochemical applications. *Journal of Molecular Liquids* **2020**, *319*, 114198.
- (52) Khandelwal, S.; Tailor, Y. K.; Kumar, M. Deep eutectic solvents (DESs) as eco-friendly and sustainable solvent/catalyst systems in organic transformations. *Journal of Molecular Liquids* **2016**, *215*, 345-386.
- (53) Mbous, Y. P.; Hayyan, M.; Hayyan, A.; Wong, W. F.; Hashim, M. A.; Looi, C. Y. Applications of deep eutectic solvents in biotechnology and bioengineering—Promises and challenges. *Biotechnology advances* **2017**, *35* (2), 105-134.
- (54) Heydari Dokoochaki, M.; Mohammadpour, F.; Zolghadr, A. R. Dye-Sensitized Solar Cells Based on Deep Eutectic Solvent Electrolytes: Insights from Experiment and Simulation. *The Journal of Physical Chemistry C* **2021**, *125* (28), 15155-15165.
- (55) Halder, A. K.; Haghbakhsh, R.; Voroshylova, I. V.; Duarte, A. R. C.; Cordeiro, M. N. D. S. Density of Deep Eutectic Solvents: The Path Forward Cheminformatics-Driven Reliable Predictions for Mixtures. *Molecules* **2021**, *26* (19), 5779.
- (56) Alizadeh, V.; Esser, L.; Kirchner, B. How is CO₂ absorbed into a deep eutectic solvent? *The Journal of Chemical Physics* **2021**, *154* (9). DOI: 10.1063/5.0038093 (accessed 11/28/2023).
- (57) El Achkar, T.; Greige-Gerges, H.; Fourmentin, S. Basics and properties of deep eutectic solvents: a review. *Environmental Chemistry Letters* **2021**, *19* (4), 3397-3408. DOI: 10.1007/s10311-021-01225-8.
- (58) Di Carmine, G.; Abbott, A. P.; D'agostino, C. Deep eutectic solvents: alternative reaction media for organic oxidation reactions. *Reaction Chemistry & Engineering* **2021**, *6* (4), 582-598.
- (59) Azmi, S.; Koudahi, M. F.; Frackowiak, E. Reline deep eutectic solvent as a green electrolyte for electrochemical energy storage applications. *Energy & Environmental Science* **2022**, *15* (3), 1156-1171.
- (60) Nguyen, D.; Van Huynh, T.; Nguyen, V. S.; Cao, P.-L. D.; Nguyen, H. T.; Wei, T.-C.; Tran, P. H.; Nguyen, P. T. Choline chloride-based deep eutectic solvents as effective electrolytes for dye-sensitized solar cells. *RSC advances* **2021**, *11* (35), 21560-21566.
- (61) Onno, A.; Chen, C.; Koswatta, P.; Boccard, M.; Holman, Z. C. Passivation, conductivity, and selectivity in solar cell contacts: Concepts and simulations based on a unified partial-resistances framework. *Journal of Applied Physics* **2019**, *126* (18).

- (62) Shaker, L. M.; Alamiery, A.; Isahak, W. N. R. W.; Al-Azzawi, W. K. Corrosion in solar cells: challenges and solutions for enhanced performance and durability. *Journal of Optics* **2023**. DOI: 10.1007/s12596-023-01277-9.
- (63) Abbott, A. P.; Harris, R. C.; Ryder, K. S. Application of hole theory to define ionic liquids by their transport properties. *The Journal of Physical Chemistry B* **2007**, *111* (18), 4910-4913.
- (64) Marcus, Y. Properties of Deep Eutectic Solvents. In *Deep Eutectic Solvents*, Marcus, Y. Ed.; Springer International Publishing, 2019; pp 45-110.
- (65) Zhang, Q.; Vigier, K. D. O.; Royer, S.; Jérôme, F. Deep eutectic solvents: syntheses, properties and applications. *Chemical Society Reviews* **2012**, *41* (21), 7108-7146.
- (66) Hou, Y.; Gu, Y.; Zhang, S.; Yang, F.; Ding, H.; Shan, Y. Novel binary eutectic mixtures based on imidazole. *Journal of Molecular Liquids* **2008**, *143* (2-3), 154-159.
- (67) Yang, Y.-l.; Kou, Y. Determination of the Lewis acidity of ionic liquids by means of an IR spectroscopic probe. *Chemical Communications* **2004**, (2), 226-227.
- (68) Sanders, W. N.; Berger, J. E. Measurement and significance of the Hammett acidity function in nonhydroxylic solvents. *Analytical Chemistry* **1967**, *39* (12), 1473-1476.
- (69) Lin, H.; Hao, F.; Li, J. Electrolyte-dependent photovoltaic responses in dye-sensitized solar cells. *Frontiers of Optoelectronics in China* **2011**, *4*, 45-52.
- (70) Wu, J.; Lan, Z.; Lin, J.; Huang, M.; Huang, Y.; Fan, L.; Luo, G.; Lin, Y.; Xie, Y.; Wei, Y. Counter electrodes in dye-sensitized solar cells. *Chemical Society Reviews* **2017**, *46* (19), 5975-6023.
- (71) Boschloo, G. Improving the performance of dye-sensitized solar cells. *Frontiers in chemistry* **2019**, *7*, 77.
- (72) Salehi, H. S.; Moulτος, O. A.; Vlugt, T. J. Interfacial properties of hydrophobic deep eutectic solvents with water. *The Journal of Physical Chemistry B* **2021**, *125* (44), 12303-12314.
- (73) Xue, J.; Wang, J.; Feng, D.; Huang, H.; Wang, M. Processing of Functional Composite Resins Using Deep Eutectic Solvent. *Crystals* **2020**, *10* (10), 864.
- (74) Crandon, L. E.; Boenisch, K. M.; Harper, B. J.; Harper, S. L. Adaptive methodology to determine hydrophobicity of nanomaterials in situ. *PLoS One* **2020**, *15* (6), e0233844.
- (75) Lin, H.; Hao, F.; Li, J. Electrolyte-dependent photovoltaic responses in dye-sensitized solar cells. *Frontiers of Optoelectronics in China* **2011**, *4* (1), 45-52. DOI: 10.1007/s12200-011-0208-Z.

- (76) Ebenezer Anitha, A.; Dotter, M. A Review on Liquid Electrolyte Stability Issues for Commercialization of Dye-Sensitized Solar Cells (DSSC). *Energies* **2023**, *16* (13), 5129.
- (77) Nguyen, D.; Nguyen, M. T.; Nguyen, T. T. D.; Huynh, V. T.; Nguyen, B. P. N.; Nguyen, P. T. Deep eutectic solvent based on choline chloride and phenol as electrolyte additives in dye-sensitized solar cells: a comparison with 4-tert-butylpyridine. *Journal of the Australian Ceramic Society* **2022**, *58* (3), 913-921.
- (78) Sharma, K.; Sharma, V.; Sharma, S. S. Dye-Sensitized Solar Cells: Fundamentals and Current Status. *Nanoscale Research Letters* **2018**, *13* (1), 381. DOI: 10.1186/s11671-018-2760-6.
- (79) Dai, Y.; van Spronsen, J.; Witkamp, G.-J.; Verpoorte, R.; Choi, Y. H. Natural deep eutectic solvents as new potential media for green technology. *Analytica chimica acta* **2013**, *766*, 61-68.
- (80) Abbott, A. P.; Boothby, D.; Capper, G.; Davies, D. L.; Rasheed, R. K. Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids. *Journal of the American Chemical Society* **2004**, *126* (29), 9142-9147.
- (81) Santana, A. P. R.; Mora-Vargas, J. A.; Guimarães, T. G. S.; Amaral, C. D. B.; Oliveira, A.; Gonzalez, M. H. Sustainable synthesis of natural deep eutectic solvents (NADES) by different methods. *Journal of Molecular Liquids* **2019**, *293*, 111452. DOI: <https://doi.org/10.1016/j.molliq.2019.111452>.
- (82) Shaibuna, M.; Abbas, A.; Kuniyil, M. J. K.; Sreekumar, K. Sustainable synthesis of 1, 8-dioxooctahydroxanthenes in deep eutectic solvents (DESS). *New Journal of Chemistry* **2021**, *45* (18), 8335-8344.
- (83) Wang, Z.; Li, S.; Li, T.; Hu, T.; Ge, X. Deep eutectic solvents (DESS) for green recycling of wasted lithium-ion batteries (LIBs): progress on pushing the overall efficiency. *Mining, Metallurgy & Exploration* **2022**, *39* (5), 2149-2165.
- (84) Zhang, C.; Fu, Y.; Gao, W.; Bai, T.; Cao, T.; Jin, J.; Xin, B. Deep Eutectic Solvent-Mediated Electrocatalysts for Water Splitting. *Molecules* **2022**, *27* (22), 8098.
- (85) Yu, D.; Xue, Z.; Mu, T. Deep eutectic solvents as a green toolbox for synthesis. *Cell Reports Physical Science* **2022**.
- (86) Liu, Y.; Friesen, J. B.; McAlpine, J. B.; Lankin, D. C.; Chen, S.-N.; Pauli, G. F. Natural deep eutectic solvents: properties, applications, and perspectives. *Journal of natural products* **2018**, *81* (3), 679-690.

- (87) Paiva, A.; Craveiro, R.; Aroso, I.; Martins, M.; Reis, R. L.; Duarte, A. R. C. Natural deep eutectic solvents—solvents for the 21st century. *ACS Sustainable Chemistry & Engineering* **2014**, *2* (5), 1063-1071.
- (88) Nolasco, M. M.; Pedro, S. N.; Vilela, C.; Vaz, P. D.; Ribeiro-Claro, P.; Rudić, S.; Parker, S. F.; Freire, C. S.; Freire, M. G.; Silvestre, A. J. Water in deep eutectic solvents: new insights from inelastic neutron scattering spectroscopy. *Frontiers in Physics* **2022**, *10*, 834571.
- (89) Sarmad, S.; Xie, Y.; Mikkola, J.-P.; Ji, X. Screening of deep eutectic solvents (DESs) as green CO₂ sorbents: from solubility to viscosity. *New Journal of Chemistry* **2017**, *41* (1), 290-301.
- (90) Kumelan, J.; Pérez-Salado Kamps, A. I.; Tuma, D.; Maurer, G. Solubility of carbon dioxide in liquid mixtures of water+[bmim][CH₃SO₄]. *Journal of chemical & engineering data* **2011**, *56* (12), 4505-4515.
- (91) Zhang, S.; Du, M.; Shao, P.; Wang, L.; Ye, J.; Chen, J.; Chen, J. Carbonic Anhydrase Enzyme-MOFs Composite with a Superior Catalytic Performance to Promote CO₂ Absorption into Tertiary Amine Solution. *Environmental Science & Technology* **2018**, *52* (21), 12708-12716. DOI: 10.1021/acs.est.8b04671.
- (92) Lu, W.; Zhang, Y.; Zhang, J.; Xu, P. Reduction of Gas CO₂ to CO with High Selectivity by Ag Nanocube-Based Membrane Cathodes in a Photoelectrochemical System. *Industrial & Engineering Chemistry Research* **2020**, *59* (13), 5536-5545. DOI: 10.1021/acs.iecr.9b06052.
- (93) Luis, P. Use of monoethanolamine (MEA) for CO₂ capture in a global scenario: Consequences and alternatives. *Desalination* **2016**, *380*, 93-99. DOI: <https://doi.org/10.1016/j.desal.2015.08.004>.
- (94) Zhang, S.; Shen, Y.; Wang, L.; Chen, J.; Lu, Y. Phase change solvents for post-combustion CO₂ capture: Principle, advances, and challenges. *Applied Energy* **2019**, *239*, 876-897. DOI: <https://doi.org/10.1016/j.apenergy.2019.01.242>.
- (95) Pishro, K. A.; Murshid, G.; Mjalli, F. S.; Naser, J. Carbon dioxide solubility in amine-based deep eutectic solvents: Experimental and theoretical investigation. *Journal of Molecular Liquids* **2021**, *325*, 115133. DOI: <https://doi.org/10.1016/j.molliq.2020.115133>.
- (96) Haider, M. B.; Kumar, R. Solubility of CO₂ and CH₄ in sterically hindered amine-based deep eutectic solvents. *Separation and Purification Technology* **2020**, *248*, 117055. DOI: <https://doi.org/10.1016/j.seppur.2020.117055>.

- (97) Pérez-Gallent, E.; Vankani, C.; Sánchez-Martínez, C.; Anastasopol, A.; Goetheer, E. Integrating CO₂ Capture with Electrochemical Conversion Using Amine-Based Capture Solvents as Electrolytes. *Industrial & Engineering Chemistry Research* **2021**, *60* (11), 4269-4278. DOI: 10.1021/acs.iecr.0c05848.
- (98) Ahmad, N.; Wang, X.; Sun, P.; Chen, Y.; Rehman, F.; Xu, J.; Xu, X. Electrochemical CO₂ reduction to CO facilitated by MDEA-based deep eutectic solvent in aqueous solution. *Renewable Energy* **2021**, *177*, 23-33.
- (99) Abdelaziz, A.; Bouzzine, S. M.; Hamidi, M. Computational investigation of dyes-sensitized solar cells containing various π -bridges achieving high photovoltaic performance with triazatruxene-based dyes. *Journal of Photochemistry and Photobiology A: Chemistry* **2024**, *447*, 115192.
- (100) Imteyaz, S.; Suresh, C. M.; Kausar, T.; Ingole, P. P. Carbon dioxide capture and its electrochemical reduction study in deep eutectic solvent (DES) via experimental and molecular simulation approaches. *Journal of CO₂ Utilization* **2023**, *68*, 102349.
- (101) Vu, Q. T.; Yamada, H.; Yogo, K. Exploring the Role of Imidazoles in Amine-Impregnated Mesoporous Silica for CO₂ Capture. *Industrial & Engineering Chemistry Research* **2018**, *57* (7), 2638-2644. DOI: 10.1021/acs.iecr.7b04722.
- (102) Cao, L.; Huang, J.; Zhang, X.; Zhang, S.; Gao, J.; Zeng, S. Imidazole tailored deep eutectic solvents for CO₂ capture enhanced by hydrogen bonds. *Physical Chemistry Chemical Physics* **2015**, *17* (41), 27306-27316.
- (103) Evjen, S.; Fiksdahl, A.; Knuutila, H. K. High-capacity amine-imidazole solvent blends for CO₂ capture. *Industrial & Engineering Chemistry Research* **2019**, *58* (24), 10533-10539.
- (104) Boualavong, J.; Gorski, C. A. Electrochemically Mediated CO₂ Capture Using Aqueous Cu(II)/Cu(I) Imidazole Complexes. *ACS ES&T Engineering* **2021**, *1* (7), 1084-1093. DOI: 10.1021/acsestengg.1c00068.
- (105) Li, X.; Hou, M.; Han, B.; Wang, X.; Zou, L. Solubility of CO₂ in a choline chloride+ urea eutectic mixture. *Journal of Chemical & Engineering Data* **2008**, *53* (2), 548-550.
- (106) Ali, E.; Hadj-Kali, M. K.; Mulyono, S.; Alnashef, I.; Fakeeha, A.; Mjalli, F.; Hayyan, A. Solubility of CO₂ in deep eutectic solvents: Experiments and modelling using the Peng–Robinson equation of state. *Chemical Engineering Research and Design* **2014**, *92* (10), 1898-1906.

- (107) Leron, R. B.; Li, M.-H. Solubility of carbon dioxide in a choline chloride–ethylene glycol based deep eutectic solvent. *Thermochimica acta* **2013**, *551*, 14-19.
- (108) Leron, R. B.; Caparanga, A.; Li, M.-H. Carbon dioxide solubility in a deep eutectic solvent based on choline chloride and urea at T= 303.15–343.15 K and moderate pressures. *Journal of the Taiwan Institute of Chemical Engineers* **2013**, *44* (6), 879-885.
- (109) Li, G.; Deng, D.; Chen, Y.; Shan, H.; Ai, N. Solubilities and thermodynamic properties of CO₂ in choline-chloride based deep eutectic solvents. *The Journal of Chemical Thermodynamics* **2014**, *75*, 58-62.
- (110) Francisco, M.; van den Bruinhorst, A.; Zubeir, L. F.; Peters, C. J.; Kroon, M. C. A new low transition temperature mixture (LTTM) formed by choline chloride+ lactic acid: Characterization as solvent for CO₂ capture. *Fluid Phase Equilibria* **2013**, *340*, 77-84.
- (111) Sze, L. L.; Pandey, S.; Ravula, S.; Pandey, S.; Zhao, H.; Baker, G. A.; Baker, S. N. Ternary deep eutectic solvents tasked for carbon dioxide capture. *ACS Sustainable Chemistry & Engineering* **2014**, *2* (9), 2117-2123.
- (112) Hsu, Y.-H.; Leron, R. B.; Li, M.-H. Solubility of carbon dioxide in aqueous mixtures of (reline+ monoethanolamine) at T=(313.2 to 353.2) K. *The Journal of Chemical Thermodynamics* **2014**, *72*, 94-99.
- (113) Trivedi, T. J.; Lee, J. H.; Lee, H. J.; Jeong, Y. K.; Choi, J. W. Deep eutectic solvents as attractive media for CO₂ capture. *Green Chemistry* **2016**, *18* (9), 2834-2842.
- (114) Haider, M. B.; Jha, D.; Marriyappan Sivagnanam, B.; Kumar, R. Thermodynamic and kinetic studies of CO₂ capture by glycol and amine-based deep eutectic solvents. *Journal of Chemical & Engineering Data* **2018**, *63* (8), 2671-2680.
- (115) Mukesh, C.; Khokarale, S. G.; Virtanen, P.; Mikkola, J.-P. Rapid desorption of CO₂ from deep eutectic solvents based on polyamines at lower temperatures: An alternative technology with industrial potential. *Sustainable Energy & Fuels* **2019**, *3* (8), 2125-2134.
- (116) Wang, C.; Mahurin, S. M.; Luo, H.; Baker, G. A.; Li, H.; Dai, S. Reversible and robust CO₂ capture by equimolar task-specific ionic liquid–superbase mixtures. *Green Chemistry* **2010**, *12* (5), 870-874.
- (117) Chen, Y.; Ai, N.; Li, G.; Shan, H.; Cui, Y.; Deng, D. Solubilities of carbon dioxide in eutectic mixtures of choline chloride and dihydric alcohols. *Journal of Chemical & Engineering Data* **2014**, *59* (4), 1247-1253.

- (118) Leron, R. B.; Li, M.-H. Solubility of carbon dioxide in a eutectic mixture of choline chloride and glycerol at moderate pressures. *The Journal of Chemical Thermodynamics* **2013**, *57*, 131-136.
- (119) Yang, Z.-Z.; He, L.-N.; Zhao, Y.-N.; Li, B.; Yu, B. CO₂ capture and activation by superbase/polyethylene glycol and its subsequent conversion. *Energy & Environmental Science* **2011**, *4* (10), 3971-3975.
- (120) Averill, B. *General chemistry: principles, patterns, and applications*; 2011.
- (121) Marcus, Y. Gas solubilities in deep eutectic solvents. *Monatshefte für Chemie-Chemical Monthly* **2018**, *149*, 211-217.
- (122) Tanaka, E.; Robertson, N. Polyiodide solid-state dye-sensitized solar cell produced from a standard liquid I⁻/I₃⁻ electrolyte. *Journal of Materials Chemistry A* **2020**, *8* (38), 19991-19999.
- (123) Tontapha, S.; Uppachai, P.; Amornkitbamrung, V. Fabrication of functional materials for dye-sensitized solar cells. *Frontiers in Energy Research* **2021**, *9*, 641983.
- (124) Ong, W.-J.; Tan, L.-L.; Chai, S.-P.; Yong, S.-T.; Mohamed, A. R. Self-assembly of nitrogen-doped TiO₂ with exposed {001} facets on a graphene scaffold as photo-active hybrid nanostructures for reduction of carbon dioxide to methane. *Nano Research* **2014**, *7*, 1528-1547.
- (125) Indrakanti, V. P.; Kubicki, J. D.; Schobert, H. H. Photoinduced activation of CO₂ on Ti-based heterogeneous catalysts: Current state, chemical physics-based insights and outlook. *Energy & Environmental Science* **2009**, *2* (7), 745-758.
- (126) Muchuweni, E.; Martincigh, B. S.; Nyamori, V. O. Recent advances in graphene-based materials for dye-sensitized solar cell fabrication. *RSC advances* **2020**, *10* (72), 44453-44469.
- (127) Baby, R.; Nixon, P. D.; Kumar, N. M.; Subathra, M.; Ananthi, N. A comprehensive review of dye-sensitized solar cell optimal fabrication conditions, natural dye selection, and application-based future perspectives. *Environmental Science and Pollution Research* **2022**, 1-34.
- (128) Castillo-Robles, J. A.; Rocha-Rangel, E.; Ramírez-de-León, J. A.; Caballero-Rico, F. C.; Armendáriz-Mireles, E. N. Advances on Dye-Sensitized Solar Cells (DSSCs) Nanostructures and Natural Colorants: A Review. *Journal of Composites Science* **2021**, *5* (11), 288.
- (129) Tomé, L. I.; Baião, V.; da Silva, W.; Brett, C. M. Deep eutectic solvents for the production and application of new materials. *Applied Materials Today* **2018**, *10*, 30-50.
- (130) Aresta, M.; Dibenedetto, A.; Angelini, A. The use of solar energy can enhance the conversion of carbon dioxide into energy-rich products: stepping towards artificial

photosynthesis. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **2013**, 371 (1996), 20120111.

(131) Wu, X.-F.; Zheng, F. Synthesis of carboxylic acids and esters from CO₂. *Chemical Transformations of Carbon Dioxide* **2018**, 1-60.

(132) Iglesias, J.; Martínez-Salazar, I.; Maireles-Torres, P.; Alonso, D. M.; Mariscal, R.; Granados, M. L. Advances in catalytic routes for the production of carboxylic acids from biomass: a step forward for sustainable polymers. *Chemical Society Reviews* **2020**, 49 (16), 5704-5771.

(133) Li, J.; Meng, C.; Gu, J.; Wang, H.; Dai, R.; Sha, H.; Zhu, H. High faradic efficiency of CO₂ conversion to formic acid catalyzed by Cu₂O hollow-dices. *Carbon Neutrality* **2022**, 1 (1), 36. DOI: 10.1007/s43979-022-00037-1.

(134) Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature* **1979**, 277 (5698), 637-638.

(135) Tu, W.; Zhou, Y.; Zou, Z. Photocatalytic conversion of CO₂ into renewable hydrocarbon fuels: state-of-the-art accomplishment, challenges, and prospects. *Advanced Materials* **2014**, 26 (27), 4607-4626.

(136) Fujita, E. Photochemical carbon dioxide reduction with metal complexes. *Coordination chemistry reviews* **1999**, 185, 373-384.

(137) Yu, Y.; Zhang, Z.; Yin, X.; Kvit, A.; Liao, Q.; Kang, Z.; Yan, X.; Zhang, Y.; Wang, X. Enhanced photoelectrochemical efficiency and stability using a conformal TiO₂ film on a black silicon photoanode. *Nature Energy* **2017**, 2 (6), 1-7.

(138) Reyes, L.; Nikitine, C.; Vilcocq, L.; Fongarland, P. Green is the new black—a review of technologies for carboxylic acid recovery from black liquor. *Green Chemistry* **2020**, 22 (23), 8097-8115.

(139) Samanta, S.; Srivastava, R. Catalytic conversion of CO₂ to chemicals and fuels: the collective thermocatalytic/photocatalytic/electrocatalytic approach with graphitic carbon nitride. *Materials Advances* **2020**, 1 (6), 1506-1545.

(140) Zhang, Q.; Yang, C.; Guan, A.; Kan, M.; Zheng, G. Photocatalytic CO₂ conversion: from C₁ products to multi-carbon oxygenates. *Nanoscale* **2022**.

(141) Aresta, M.; Dibenedetto, A.; Angelini, A. The changing paradigm in CO₂ utilization. *J. CO₂ Util.* 3–4, 65–73. 2013.

- (142) Boldrini, C. L.; Quivelli, A. F.; Manfredi, N.; Capriati, V.; Abbotto, A. Deep Eutectic Solvents in Solar Energy Technologies. *Molecules* **2022**, *27* (3), 709.
- (143) O'regan, B.; Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *nature* **1991**, *353* (6346), 737-740.
- (144) Li, C. T.; Lin, R. Y. Y.; Lin, J. T. Sensitizers for Aqueous-Based Solar Cells. *Chemistry—An Asian Journal* **2017**, *12* (5), 486-496.
- (145) Jiang, X.; Marinado, T.; Gabrielsson, E.; Hagberg, D. P.; Sun, L.; Hagfeldt, A. Structural Modification of Organic Dyes for Efficient Coadsorbent-Free Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry C* **2010**, *114* (6), 2799-2805. DOI: 10.1021/jp908552t.
- (146) Feldt, S. M.; Gibson, E. A.; Gabrielsson, E.; Sun, L.; Boschloo, G.; Hagfeldt, A. Design of Organic Dyes and Cobalt Polypyridine Redox Mediators for High-Efficiency Dye-Sensitized Solar Cells. *Journal of the American Chemical Society* **2010**, *132* (46), 16714-16724. DOI: 10.1021/ja1088869.
- (147) Kakiage, K.; Aoyama, Y.; Yano, T.; Otsuka, T.; Kyomen, T.; Unno, M.; Hanaya, M. An achievement of over 12 percent efficiency in an organic dye-sensitized solar cell. *Chemical Communications* **2014**, *50* (48), 6379-6381.
- (148) Kokkonen, M.; Talebi, P.; Zhou, J.; Asgari, S.; Soomro, S. A.; Elsehrawy, F.; Halme, J.; Ahmad, S.; Hagfeldt, A.; Hashmi, S. G. Advanced research trends in dye-sensitized solar cells. *Journal of Materials Chemistry A* **2021**, *9* (17), 10527-10545.
- (149) Zhang, S.; Jin, J.; Li, D.; Fu, Z.; Gao, S.; Cheng, S.; Yu, X.; Xiong, Y. Increased power conversion efficiency of dye-sensitized solar cells with counter electrodes based on carbon materials. *RSC advances* **2019**, *9* (38), 22092-22100.
- (150) Li, Y., X. Li, and Y. Xu, Theoretical insights into the effect of pristine, doped and hole graphene on the overall performance of dye-sensitized solar cells. *Inorganic Chemistry Frontiers*, 2020. 7(1): p. 157-168.
- (151) Gao, F., et al., Theoretical studies on the possible sensitizers of DSSC: nanocomposites of graphene quantum dot hybrid phthalocyanine/tetrabenzoporphyrin/tetrabenzotriazaporphyrins/cis-tetrabenzodiazaporphyrins/tetrabenzomonoazaporphyrins and their Cu-metallated macrocycles. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2018. 195: p. 176-183.

- (152) Rezvani, M., M.D. Ganji, S. Jameh-Bozorgi, and A. Niazi, DFT/TD-semiempirical study on the structural and electronic properties and absorption spectra of supramolecular fullerene-porphyrine-metalloporphyrine triads based dye-sensitized solar cells. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2018. 194: p. 57-66.
- (153) Moghim, M.T., S. Jamehbozorgi, M. Rezvani, and M. Ramezani, Computational investigation on the geometry and electronic structures and absorption spectra of metal-porphyrin-oligo-phenyleneethynylenes-[60] fullerene triads. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2022. 280: p. 121488.
- (154) Fina, J., et al., Enhancing Light Harvesting in Dye-Sensitized Solar Cells through Mesoporous Silica Nanoparticle-Mediated Diffuse Scattering Back Reflectors. *Electronic Materials*, 2023. 4(3): p. 124-135.
- (155) Tomasi, S., S. Baghbanzadeh, S. Rahimi-Keshari, and I. Kassal, Coherent and controllable enhancement of light-harvesting efficiency. *Physical Review A*, 2019. 100(4): p. 043411.
- (156) Ganji, M.D., M. Rezvani, and S. Tanreh, Characterization and theoretical modeling of solar cells. *Fundamentals of Solar Cell Design*, 2021: p. 169-215.
- (157) Bittner, J. P.; Zhang, N.; Huang, L.; de María, P. D.; Jakobtorweihen, S.; Kara, S. Impact of deep eutectic solvents (DESs) and individual DES components on alcohol dehydrogenase catalysis: connecting experimental data and molecular dynamics simulations. *Green Chemistry* 2022, 24 (3), 1120-1131.
- (158) Iftikhar, H.; Sonai, G. G.; Hashmi, S. G.; Nogueira, A. F.; Lund, P. D. Progress on Electrolytes Development in Dye-Sensitized Solar Cells. *Materials* 2019, 12 (12), 1998.
- (159) Boldrini, C. L.; Manfredi, N.; Perna, F. M.; Capriati, V.; Abboto, A. Eco-friendly sugar-based natural deep eutectic solvents as effective electrolyte solutions for dye-sensitized solar cells. *ChemElectroChem* 2020, 7 (7), 1707-1712.
- (160) Cruz, H.; Pinto, A. L.; Jordão, N.; Neves, L. A.; Branco, L. C. Alkali Iodide Deep Eutectic Solvents as Alternative Electrolytes for Dye Sensitized Solar Cells. *Sustainable Chemistry* 2021, 2 (2), 222-236.

- (161) Steparuk, A. S.; Irgashev, R. A.; Zhilina, E. F.; Emets, V. V.; Grinberg, V. A.; Krivogina, E. V.; Belova, E. V.; Lazarenko, P. I.; Rusinov, G. L.; Kozyukhin, S. A. Performance evaluation of dye-sensitized solar cells (DSSCs) based on metal-free thieno[3,2-b]indole dyes. *Journal of Materials Science: Materials in Electronics* 2022, 33 (9), 6307-6317. DOI: 10.1007/s10854-022-07805-w.
- (162) Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Grätzel, M. Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency. *science* 2011, 334 (6056), 629-634.
- (163) Yella, A.; Humphry-Baker, R.; Curchod, B. F. E.; Ashari Astani, N.; Teuscher, J.; Polander, L. E.; Mathew, S.; Moser, J.-E.; Tavernelli, I.; Rothlisberger, U.; et al. Molecular Engineering of a Fluorene Donor for Dye-Sensitized Solar Cells. *Chemistry of Materials* 2013, 25 (13), 2733-2739. DOI: 10.1021/cm401593b.
- (164) Cassone, G.; Calogero, G.; Sponer, J.; Saija, F. Mobilities of iodide anions in aqueous solutions for applications in natural dye-sensitized solar cells. *Physical Chemistry Chemical Physics* 2018, 20 (18), 13038-13046.
- (165) Cassone, G.; Creazzo, F.; Giaquinta, P. V.; Saija, F.; Saitta, A. M. Ab initio molecular dynamics study of an aqueous NaCl solution under an electric field. *Physical Chemistry Chemical Physics* 2016, 18 (33), 23164-23173.
- (166) Cassone, G.; Creazzo, F.; Giaquinta, P. V.; Sponer, J.; Saija, F. Ionic diffusion and proton transfer in aqueous solutions of alkali metal salts. *Physical Chemistry Chemical Physics* 2017, 19 (31), 20420-20429.
- (167) Nguyen, D., et al., Choline chloride-based deep eutectic solvents as effective electrolytes for dye-sensitized solar cells. *RSC advances*, 2021. 11(35): p. 21560-21566.
- (168) Nahar, Y. and S.C. Thickett, Greener, Faster, Stronger: The Benefits of Deep Eutectic Solvents in Polymer and Materials Science. *Polymers*, 2021. 13(3): p. 447.

RSC Advances

Guidelines for Reviewers



Thank you very much for agreeing to review this manuscript for [RSC Advances](#).

The criteria for publication are that the work must be high quality, well conducted and advance the development of the field.

Please consider RSC Advances' scope criteria when making your recommendation:

- Work should contain chemistry, or be of relevance to chemists
- Work should provide an insight that advances the chemistry field

Papers that contain little or no chemistry and are not considered to be of interest or relevance to the chemistry community are not within the scope of the journal.

The following manuscript has been submitted for consideration as a

REVIEW

When making your recommendation, please consider the following:

- Reviews should present an advance over the existing literature
- Reviews should be easily comprehensible to a non-specialist in the field
- Reviews should not contain any original research

Please inform the editor if the work, or a significant part of the work, has previously been published or represents part of an unduly fragmented investigation.

Please contact us if there are any conflicts of interest or there is a significant part of the work you are unable to referee with confidence.

PLEASE NOTE: RSC Advances offers authors the option of transparent peer review (TPR). If authors choose TPR, the reviewers' comments, authors' response and editor's decision letter for all stages of review are also published if the article is accepted. Reviewers will remain anonymous unless they choose to sign their report and only comments to the authors will be published – confidential comments to the editor will not be published.

Please note by peer reviewing you give consent to your anonymised report being published if authors have selected transparent peer review.

Best regards,

Professor Russell Cox
Editor-in-Chief
Leibniz Universität Hannover

Professor Karen Faulds
Editor-in-Chief
University of Strathclyde

Dr Laura Fisher
Executive Editor
Royal Society of Chemistry

Contact us

Please visit our [reviewer hub](#) for further details of our processes, policies and reviewer responsibilities as well as guidance on how to review, or click the links below.





UNIVERSIDADE ESTADUAL PAULISTA
"JÚLIO DE MESQUITA FILHO"
Câmpus de São José do Rio Preto

São José do Rio Preto, 04 April 2024

Dr Lei Li

Associate Editor, RSC Advances

We are pleased to present the second reviewed version of the manuscript entitled "*Use of deep eutectic solvents in environmentally-friendly dye-sensitized solar cells and their physicochemical properties: A brief review*" manuscript Number: RA-REV-03-2024-001610.R1. The manuscript was reviewed and all corrections and suggestions were taken into account and are highlighted in yellow in the corrected version. Please, find below the answers for the referee queries/comments.

We thank you very much for the opportunity and suggestions to improve the manuscript and its impact. We are also thankful for your kind editorial assistance and time, and we hope that the revised manuscript is in the desired quality.

Yours sincerely,

Professor Mario Henrique Gonzalez
São Paulo State University (UNESP)
mario.gonzalez@unesp.br

Answers to reviewer's comments

REVIEWER 1:

Reviewer #1: The authors have addressed all criticized points and revised the manuscript accordingly. The article can now be accepted for publication.

Answer: We appreciate your revisions and your valuable feedback on our manuscript.

REVIEWER 1:

Reviewer #2: In the previous round and revising the manuscript accordingly. However, after having checked the revised manuscript, there are still the minor issues that should be well addressed. Even though the authors cited and added three figures in the updated manuscript, that was not that enough. More related figures from the previously published papers should be added, in particular for the sections of properties and characteristics of DESs, preparation of DESs, and some other sections.

Answer: Thank you for your continued engagement with our manuscript. We appreciate your feedback and acknowledge the effort you've put into reviewing our work. We have carefully considered your comments and made further revisions to address the minor issues you highlighted. Additionally, we have incorporated three new figures as requested as highlighted. However, we understand that more related figures from previously published papers would enhance the clarity and depth of our manuscript.

In light of your valuable input, we will diligently search for relevant figures to supplement the sections on properties and characteristics of DESs, as well as the preparation of DESs. Your guidance will undoubtedly contribute to improving the overall quality of our work.

Thank you once again for your thorough review and we remain committed to refining our manuscript to meet the highest standards.

For Review-type articles only:

- A photograph and biography of yourself and your co-authors. Separate photographs of each author may be supplied or if you prefer, a group photograph, saved as a .tif, .pdf or .jpeg file. The resolution of the photographs should be 600 dpi or higher.



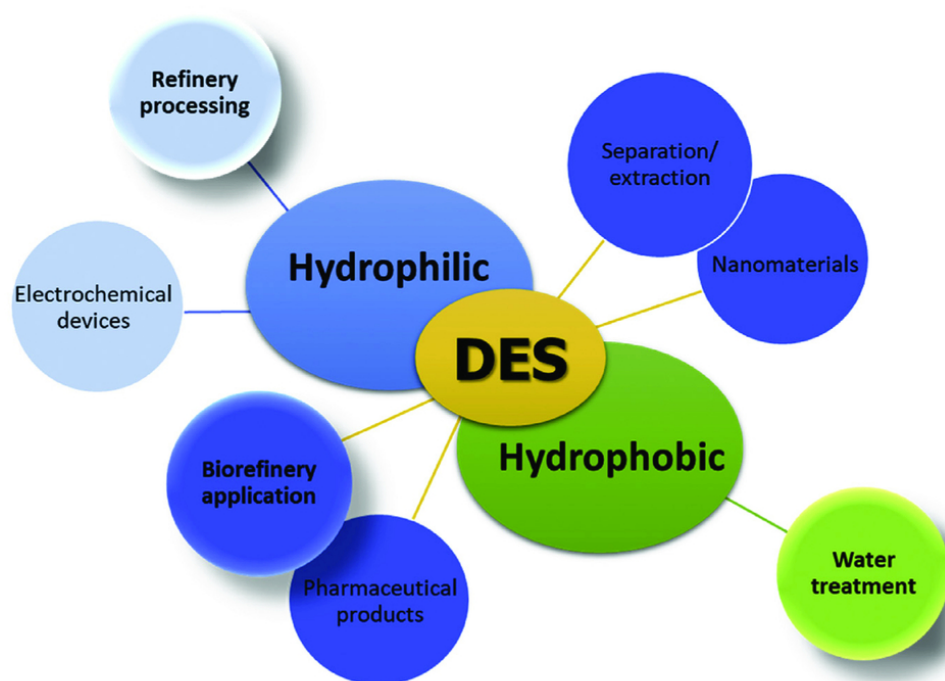
UNIVERSIDADE ESTADUAL PAULISTA
"JÚLIO DE MESQUITA FILHO"
Câmpus de São José do Rio Preto

Biography

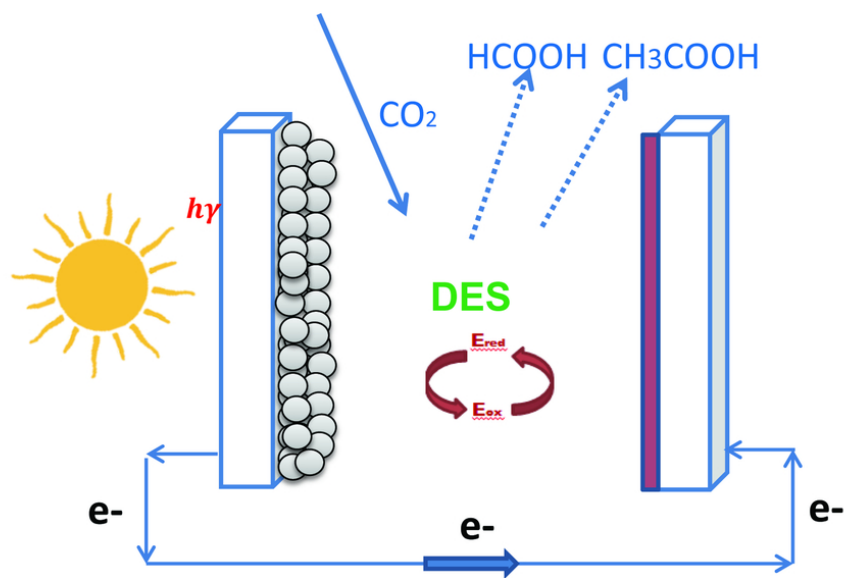
Khatereh A. Pishro, Ph.D., is doing a postdoc at the Institute of Biosciences, Letters, and Exact Sciences (IBILCE) of the State University of São Paulo (UNESP), S. J. do Rio Preto, SP, Brazil. Possess a Ph.D. degree in chemical engineering from Sultan Qaboos University in Oman at the Petroleum and Chemical Engineering Department (2021), a Master's degree in Chemical Engineering with a concentration in Biotechnology, and a Bachelor's degree in Applied Chemistry. Focused on environmental chemistry, ion liquids, deep eutectic solvents, theoretical studies, and simulations. The primary focus is on green chemistry, solid-phase extraction, chromatographic analysis, chemical separation, global warming, CO₂ capture, formulation, sample preparation, and analytical instruments.

Biography

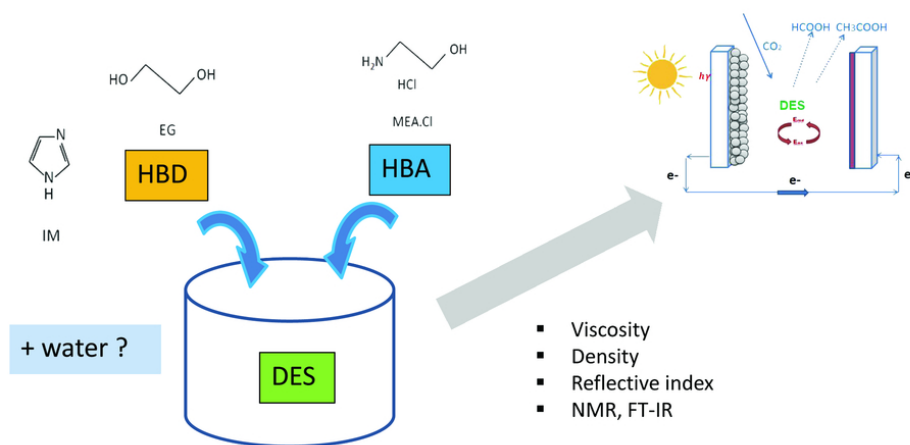
Mario Henrique Gonzalez, Ph.D., is Full Professor at the São Paulo State University (UNESP), - UNESP in the Department of Chemistry and Environmental Sciences (DQCA). I'm graduated in Chemistry from the Federal University of São Carlos, Department of Chemistry (2004), the title of Master of Science of the University of São Paulo (IQSC-USP), by the Institute of Chemistry of São Carlos in 2007. I developed my Ph.D. in the analytical chemistry concentration area, with a sandwich period at Wake Forest University. I have experience in the area of Analytical Chemistry, Green Chemistry and Environmental Chemistry, mainly in the following topics: Spectroanalytical Techniques, Chromatographic Analysis and Chemical Separations, Trace Determination, Waste Treatment, Sample Preparation using Microwave Radiation, Chemical Speciation, Bioaccumulation and Analytical Instrumentation. I'm a coordinator by the Green Analytical Chemistry Innovation Group (GIQAV) in the Department of Chemistry and Environmental Sciences at UNESP.



82x58mm (300 x 300 DPI)



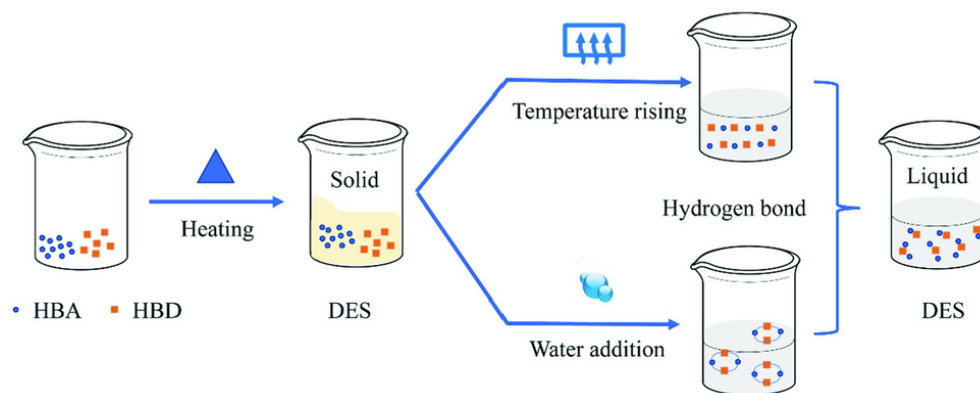
82x60mm (300 x 300 DPI)



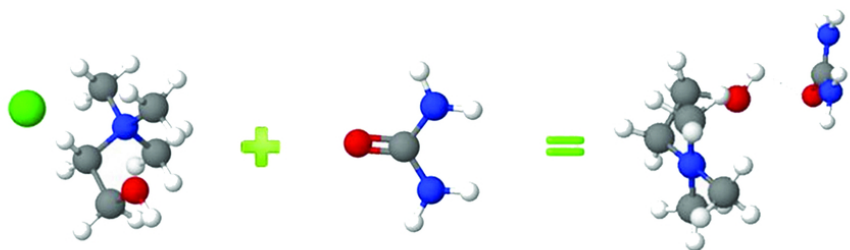
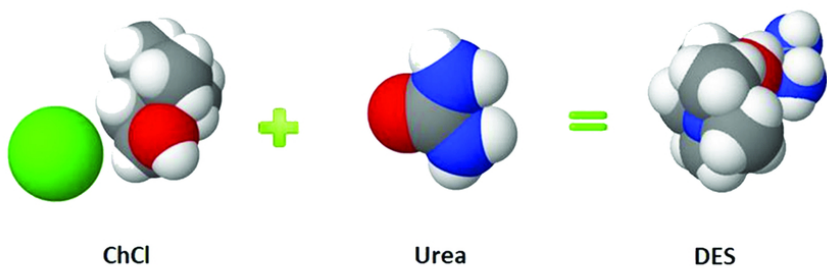
82x46mm (300 x 300 DPI)



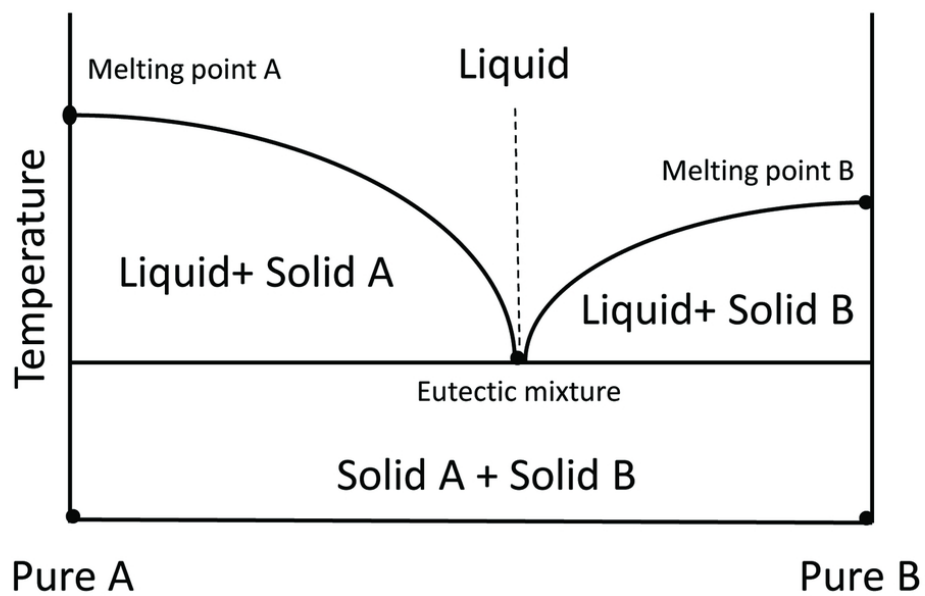
42x49mm (300 x 300 DPI)



82x33mm (300 x 300 DPI)

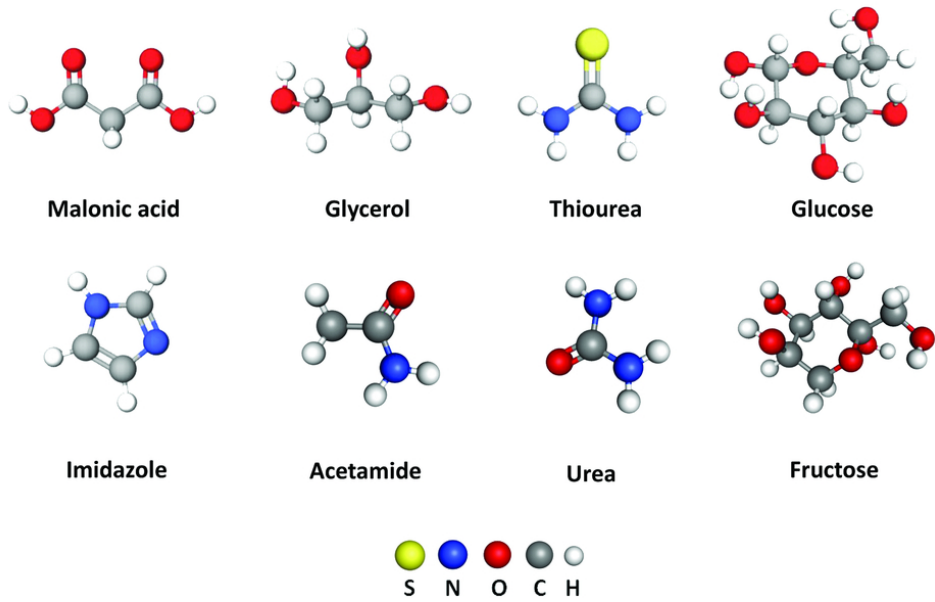


82x49mm (300 x 300 DPI)



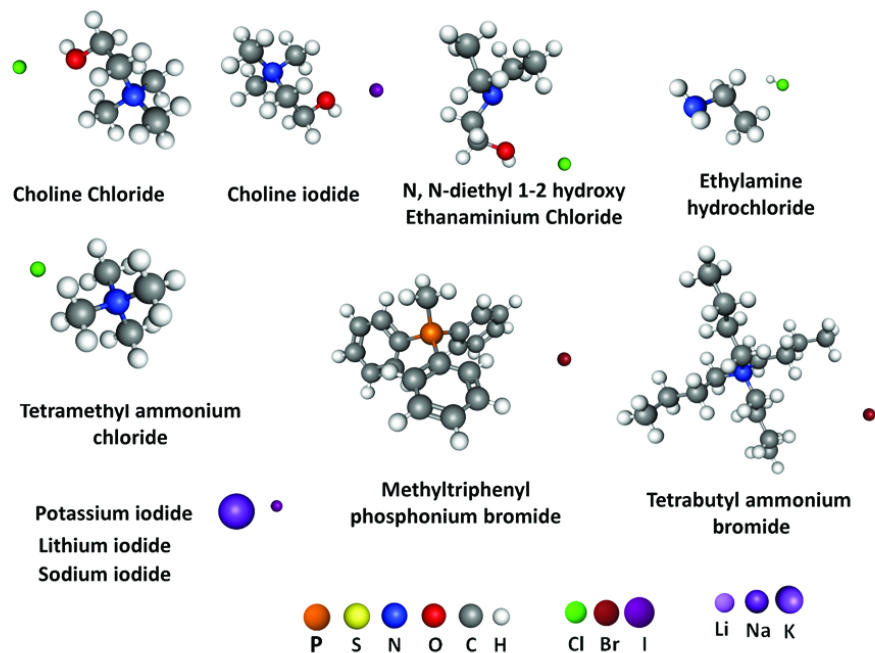
82x60mm (300 x 300 DPI)

Hydrogen Bond Donors (HBDs)

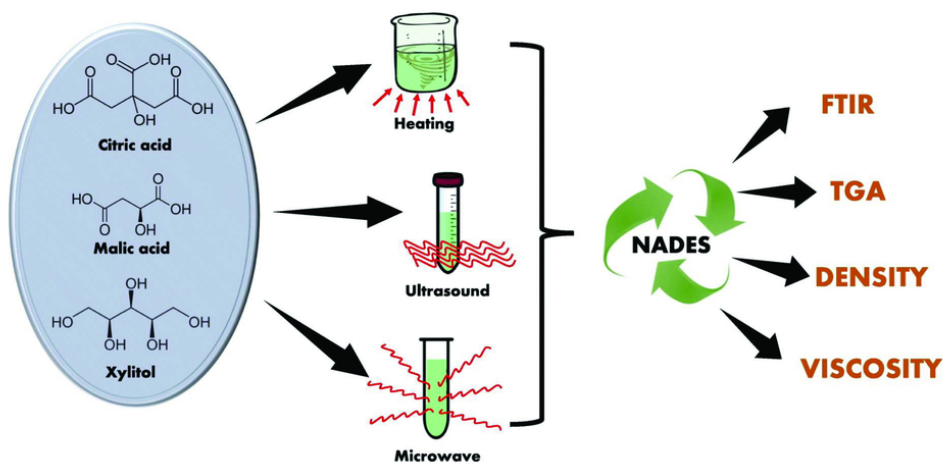


82x60mm (300 x 300 DPI)

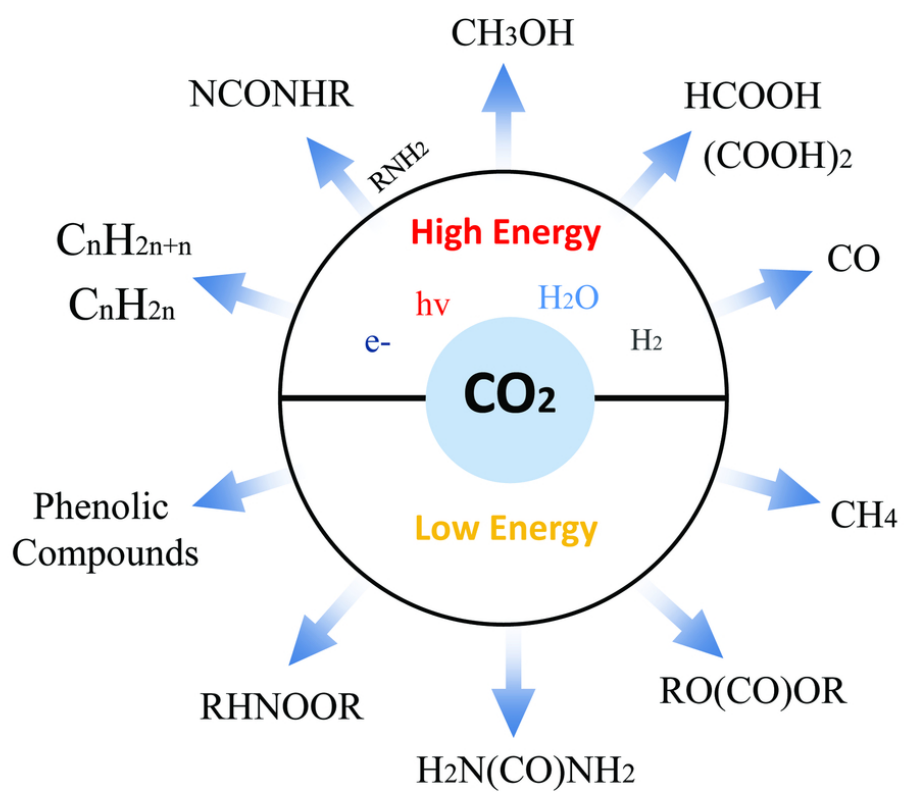
Hydrogen Bond Acceptors (HBAs)



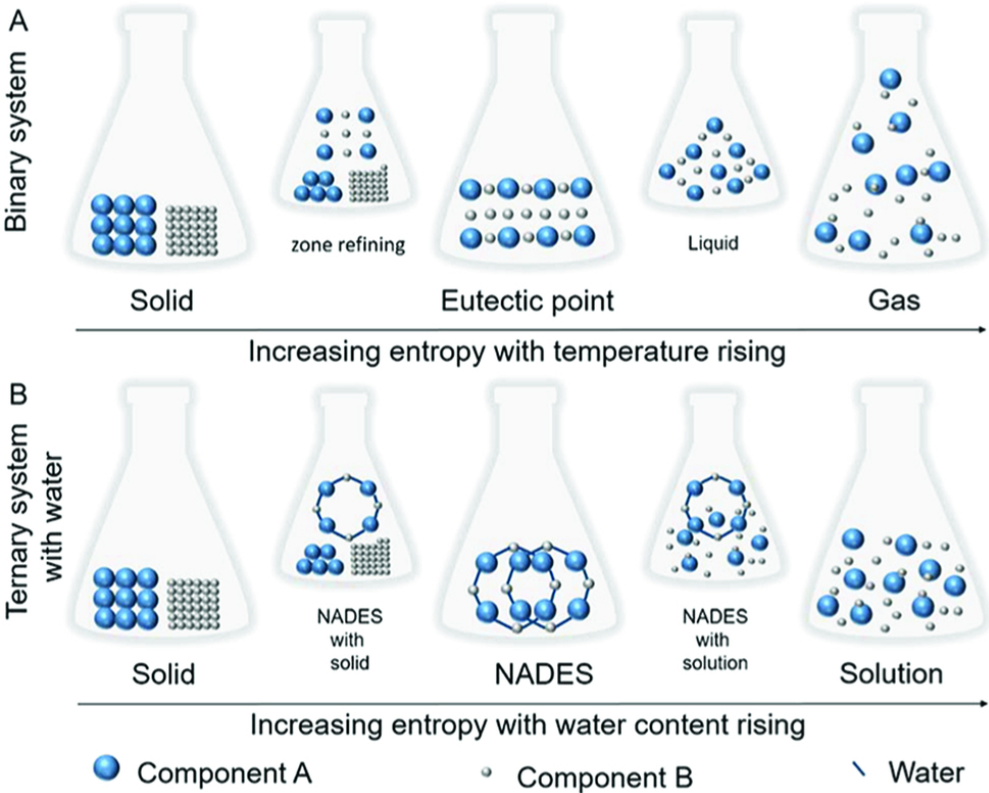
82x62mm (300 x 300 DPI)



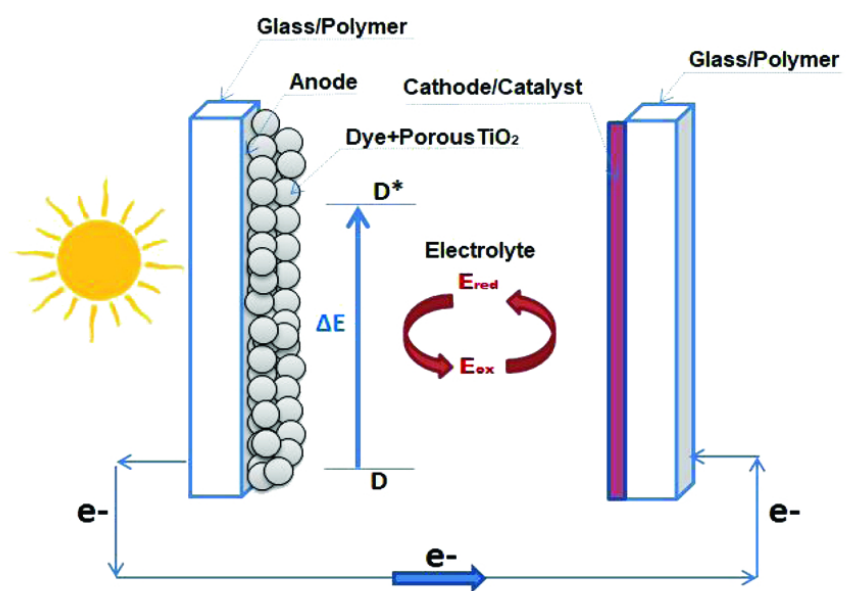
82x47mm (300 x 300 DPI)



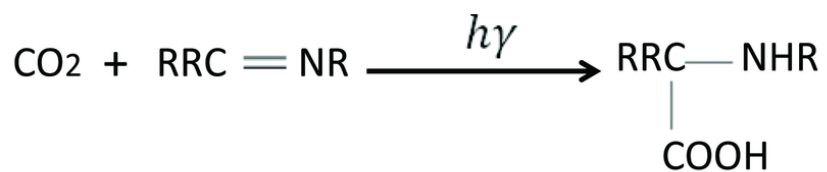
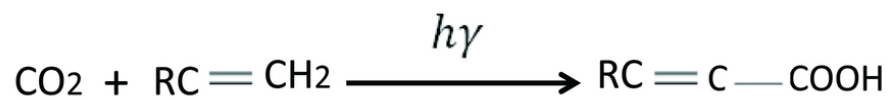
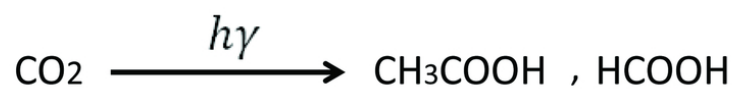
82x72mm (300 x 300 DPI)



82x66mm (300 x 300 DPI)



82x62mm (300 x 300 DPI)



82x48mm (300 x 300 DPI)



451x449mm (72 x 72 DPI)

23-Mar-2024

Dear Dr Gonzalez:

Manuscript ID: RA-REV-03-2024-001610.R1

TITLE: Use of deep eutectic solvents in environmentally-friendly dye-sensitized solar cells and their physicochemical properties: A brief review

Thank you for your submission to RSC Advances, published by the Royal Society of Chemistry. I sent your revised manuscript to one of the original reviewers and I have now received their report which is copied below.

After careful evaluation of your manuscript and the reviewer's report, I will be pleased to accept your manuscript for publication after revisions.

Please revise your manuscript to fully address the reviewer's comments. When you submit your revised manuscript please include a point by point response to the reviewer's comments and highlight the changes you have made. Full details of the files you need to submit are listed at the end of this email.

Please submit your revised manuscript as soon as possible using this link:

*** PLEASE NOTE: This is a two-step process. After clicking on the link, you will be directed to a webpage to confirm. ***

https://mc.manuscriptcentral.com/rscadv?URL_MASK=f2396c56aa4d432793b6ae8cdc8c9fff

(This link goes straight to your account, without the need to log in to the system. For your account security you should not share this link with others.)

Alternatively, you can log in to your account (<https://mc.manuscriptcentral.com/rscadv>) where you will need your case-sensitive user ID and password details.

You should submit your revised manuscript as soon as possible; please note you will receive a series of automatic reminders. If your revisions will take a significant length of time, please contact me. If I do not hear from you, I may withdraw your manuscript from consideration and you will have to resubmit. Any resubmission will receive a new submission date.

All RSC Advances articles are published under an open access model, and the appropriate article processing charge (APC) will apply. Details of the APC and discounted rates can be found at <https://www.rsc.org/journals-books-databases/about-journals/rsc-advances/#charges-RSC-Advances>

RSC Advances strongly encourages authors of research articles to include an 'Author contributions' section in their manuscript, for publication in the final article. This should appear immediately above the 'Conflict of interest' and 'Acknowledgement' sections. I strongly recommend you use CRediT (the

Contributor Roles Taxonomy, <https://credit.niso.org/>) for standardised contribution descriptions. All authors should have agreed to their individual contributions ahead of submission and these should accurately reflect contributions to the work. Please refer to our general author guidelines <https://www.rsc.org/journals-books-databases/author-and-reviewer-hub/authors-information/responsibilities/> for more information. **The "Author Contributions section" was added to the manuscript and is highlighted.**

The Royal Society of Chemistry requires the submitting author to provide their ORCID iD when they submit a revised manuscript. This is quick and easy to do as part of the revised manuscript submission process. We will publish this information with the article, and you may choose to have your ORCID record updated automatically with details of the publication.

Please also encourage your co-authors to sign up for their own ORCID account and associate it with their account on our manuscript submission system. Please note that we are unable to do this on behalf of your co-authors. For further information see: <https://www.rsc.org/journals-books-databases/journal-authors-reviewers/processes-policies/#attribution-id>.

Please note: to support increased transparency, RSC Advances offers authors the option of transparent peer review. If authors choose this option, the reviewers' comments, authors' response and editor's decision letter for all versions of the manuscript are published alongside the article. Reviewers remain anonymous unless they choose to sign their report. We will ask you to confirm whether you would like to take up this option at the revision stages.

I look forward to receiving your revised manuscript.

Yours sincerely,
Dr Lei Li
Associate Editor, RSC Advances

REVIEWER REPORT(S):
Referee: 1

Recommendation: Accept: suitable for publication without modification

Comments:

The authors have addressed all criticized points and revised the manuscript accordingly. The article can now be accepted for publication.

#Respond to the Referee 1

We appreciate your revisions and your valuable feedback on our manuscript.

Additional Questions:

RSC Advances welcomes reviews from all areas of the chemical sciences. Review articles published in the journal must be:

- a balanced view of general interest to the journal's wide, community spanning readership.
- an authoritative, timely critique of the field's current state that justifies its necessity, while also suggesting future directions.
- accessible to the non-specialist.

Please consider these criteria carefully when you write your report.:

By submitting this review: I agree to RSC Advances' transparent peer review policy.

I understand that, if the manuscript is accepted for publication, and the authors have chosen transparent peer review, my (anonymous) reviewer report will be published, with the authors' response and the editor's decision letter, alongside the article.

I understand that my report will remain anonymous unless I insert my name in the "comments to the author" box.

I agree for my reviewer report to be made available under an Open Access Creative Commons CC-BY license.

How would you rate the significance and quality of this review?: High (suitable for RSC Advances): a comprehensive and informative review offering valuable insights and analysis that would be of interest to a wide readership

Does the Review add to the understanding or development of a chemistry-related field?: Yes

Is the article a well-balanced consideration of the subject with appropriate and balanced citations?: Yes

Does the article introduce and discuss the topic at a level intelligible to the non-specialist?: Yes

Recommendation: Minor Revisions: suitable for publication after changes

Comments:

The reviewer would like to thank the authors for having put efforts in replying to the comments raised in the previous round and revising the manuscript accordingly. However, after having checked the revised manuscript, there are still the minor issues that should be well addressed. **Even though the authors cited and added three figures in the updated manuscript, that was not that enough.** More related figures from the previously published papers should be added, **in particular for the sections of properties and characteristics of DESs, preparation of DESs, and some other sections.**

#Respond to the Referee 2

Thank you for your continued engagement with our manuscript. We appreciate your feedback and acknowledge the effort you've put into reviewing our work.

We have carefully considered your comments and made further revisions to address the minor issues you highlighted. Additionally, we have incorporated three new figures as requested as highlighted. However, we understand that more related figures from previously published papers would enhance the clarity and depth of our manuscript.

In light of your valuable input, we will diligently search for relevant figures to supplement the sections on properties and characteristics of DESs, as well as the preparation of DESs. Your guidance will undoubtedly contribute to improving the overall quality of our work.

Thank you once again for your thorough review and we remain committed to refining our manuscript to meet the highest standards.

Additional Questions:

RSC Advances welcomes reviews from all areas of the chemical sciences. Review articles published in the journal must be:

a balanced view of general interest to the journal's wide, community spanning readership.

an authoritative, timely critique of the field's current state that justifies its necessity, while also suggesting future directions.

accessible to the non-specialist.

Please consider these criteria carefully when you write your report.:

By submitting this review: I agree to RSC Advances' transparent peer review policy.

I understand that, if the manuscript is accepted for publication, and the authors have chosen transparent peer review, my (anonymous) reviewer report will be published, with the authors' response and the editor's decision letter, alongside the article.

I understand that my report will remain anonymous unless I insert my name in the "comments to the author" box.

I agree for my reviewer report to be made available under an Open Access Creative Commons CC-BY license.

How would you rate the significance and quality of this review?: High (suitable for RSC Advances): a comprehensive and informative review offering valuable insights and analysis that would be of interest to a wide readership

Does the Review add to the understanding or development of a chemistry-related field?: Yes

Is the article a well-balanced consideration of the subject with appropriate and balanced citations?: Yes

Does the article introduce and discuss the topic at a level intelligible to the non-specialist?: Yes

FILES TO PROVIDE WITH YOUR REVISED MANUSCRIPT:

IMPORTANT: Your original files are available to you when you upload your revised manuscript. Please delete any redundant files before completing the submission. Please carefully check the spelling and format of all author names, affiliations and funding information. If your paper is accepted for publication, it is important this information is accurate to ensure your article is correctly indexed, which may affect citations and future funding evaluation. Please note that if you have selected Accepted Manuscript publication, the author list will appear as provided in the ScholarOne submission details until your Advance Article is published and this information is updated from your article.

- A point-by-point response to the comments made by the reviewer(s). (If selecting transparent peer review, please copy your full response to reviewers into the "Your Response" text box provided, but do not include any salutation e.g. "Dear Editor Name").
- Your revised manuscript with any changes clearly marked (.doc(x) or .pdf file)
- Your revised manuscript as a .doc(x) file including figures, without highlighting, track changes, etc. (If providing in TeX format instead, please also provide a final PDF version including figures). Please note that we cannot proceed with publication using a .pdf file only.

High quality images

EITHER

embedded in a doc(x) file

OR

as separate numbered Figures, Schemes or Charts in .tif, .eps or .pdf format, with a resolution of 600 dpi or greater.

AND

- A table of contents entry: graphic maximum size 8 cm wide x 4 cm high and 1-2 sentence(s) of editable text, with a maximum of 250 characters (including spaces), highlighting the key findings of the work. It is recommended authors make use of the full space available for the graphic. See our Author Guidelines for more details: <https://www.rsc.org/journals-books-databases/author-and-reviewer-hub/>
- Your revised Electronic Supplementary Information (if any)
- Your revised CheckCIF reports (if any). Please ensure that any revised cif files have been deposited with the Cambridge Crystallographic Data Centre (CCDC) via <https://deposit.ccdc.cam.ac.uk/> before you submit your revised manuscript.

For Review-type articles only:

- A photograph and biography of yourself and your co-authors. Separate photographs of each author may be supplied or if you prefer, a group photograph, saved as a .tif, .pdf or .jpeg file. The resolution of the photographs should be 600 dpi or higher.

Biography

Khatereh A. Pishro, Ph.D., is doing a postdoc at the Institute of Biosciences, Letters, and Exact Sciences (IBILCE) of the State University of São Paulo (UNESP), S. J. do Rio Preto, SP, Brazil. Possess a Ph.D. degree in chemical engineering from Sultan Qaboos University in Oman at the Petroleum and Chemical Engineering Department (2021), a Master's degree in Chemical Engineering with a concentration in Biotechnology, and a Bachelor's degree in Applied Chemistry. Focused on environmental chemistry, ion liquids, deep eutectic solvents, theoretical studies, and simulations. The primary focus is on green chemistry, solid-phase extraction, chromatographic analysis, chemical separation, global warming, CO₂ capture, formulation, sample preparation, and analytical instruments.

Photography

Khatereh photo attached as a tif file .

The dimensions of the photograph in the printed journal will be 4 cm wide x 5 cm high (individual photograph) or 8.3 cm wide x 5 cm high (group photograph). Individual photographs should be accompanied by a maximum of 100 words; a group photograph by a maximum of 200 words. There can be a maximum of 6 individual biographies per article.

- Please ensure that necessary permissions are acknowledged in the figure captions in accordance with the publishers' instruction. Information on how to obtain permissions and rights that we require are given on our website at <https://www.rsc.org/journals-books-databases/journal-authors-reviewers/licences-copyright-permissions/>. Please keep a copy of any correspondence or licences relating to permissions from other publishers for possible future reference.

If you need to contact the journal, please use the email address advances@rsc.org

DISCLAIMER:

This communication is from The Royal Society of Chemistry, a company incorporated in England by Royal Charter (registered number RC000524) and a charity registered in England and Wales (charity number 207890). Registered office: Burlington House, Piccadilly, London W1J 0BA. Telephone: +44 (0) 20 7437 8656.

The content of this communication (including any attachments) is confidential, and may be privileged or contain copyright material. It may not be relied upon or disclosed to any person other than the intended recipient(s) without the consent of The Royal Society of Chemistry. If you are not the intended recipient(s), please (1) notify us immediately by replying to this email, (2) delete all copies from your system, and (3) note that disclosure, distribution, copying or use of this communication is strictly prohibited.

Any advice given by The Royal Society of Chemistry has been carefully formulated but is based on the information available to it. The Royal Society of Chemistry cannot be held responsible for accuracy or completeness of this communication or any attachment. Any views or opinions presented in this email are solely those of the author and do not represent those of The Royal Society of Chemistry. The views expressed in this communication are personal to the sender and unless specifically stated, this e-mail does not constitute any part of an offer or contract. The Royal Society of Chemistry shall not be liable for any resulting damage or loss as a result of the use of this email and/or attachments, or for the consequences of any actions taken on the basis of the information provided. The Royal Society of Chemistry does not warrant that its emails or attachments are Virus-free; The Royal Society of Chemistry has taken reasonable precautions to ensure that no viruses are contained in this email, but does not accept any responsibility once this email has been transmitted. Please rely on your own screening of electronic communication.

More information on The Royal Society of Chemistry can be found on our website: www.rsc.org

+++++