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

 Khatereh A. Pishro  and Mario Henrique Gonzalez \*

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 CO<sub>2</sub> 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 CO<sub>2</sub> 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.

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## 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.<sup>1,2</sup>

According to the Paris Agreement, urgent actions are needed to lower the emissions of CO<sub>2</sub> into the atmosphere, as they cause serious effects in the environment.<sup>3</sup> One promising solution is to use solar cells to convert CO<sub>2</sub> into valuable products such as hydrocarbons, which can also store solar energy, a plentiful, clean, and safe resource.<sup>4</sup> The conversion of CO<sub>2</sub> can help reduce greenhouse gas levels, while at the same time absorbing sunlight, contributing to mitigating global warming.<sup>5</sup>

Artificial photosynthetic systems are devices that use sunlight as an energy source and water as an electron source to convert CO<sub>2</sub> into useful chemicals (fuels or carbohydrates). This

*São Paulo State University (UNESP), Institute of Biosciences, Humanities and Exact Sciences (IBILCE), National Institute for Alternative Technologies of Detection, Toxicological Evaluation and Removal of Micropollutants and Radioactives (INCT-DATREM), São José do Rio Preto, SP, 15054-000, Brazil. E-mail: mario.gonzalez@unesp.br; Fax: +55 17 32212512; Tel: +55 17 32212512*


**Khatereh A. Pishro**

**Mario Henrique Gonzalez**


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 CO<sub>2</sub> at the cathode.<sup>6–8</sup> 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).<sup>9,10</sup> Ionic liquids (ILs) and deep eutectic solvents (DESs) have been proposed for various industrial processes and applications, such as chemical synthesis,<sup>11</sup> absorption,<sup>12</sup> biomass pretreatment,<sup>13</sup> extraction,<sup>14</sup> electrolytes for electrochemistry (fuel cells and lithium batteries),<sup>15</sup> and dye-sensitized solar cells (DSSCs).<sup>16–18</sup> Scheme 1 provides an overview of DESs applications, based on their hydrophilic and hydrophobic characteristics.<sup>19</sup>

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 production.<sup>20–24</sup>

DSSCs are based on a photoactive anode with an n-type semiconductor layer (usually TiO<sub>2</sub>) sensitized by an organometallic dye, a counter electrode, and a liquid electrolyte that completes the circuit and regenerates the dye. Liquid electrolytes<sup>25</sup> 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,

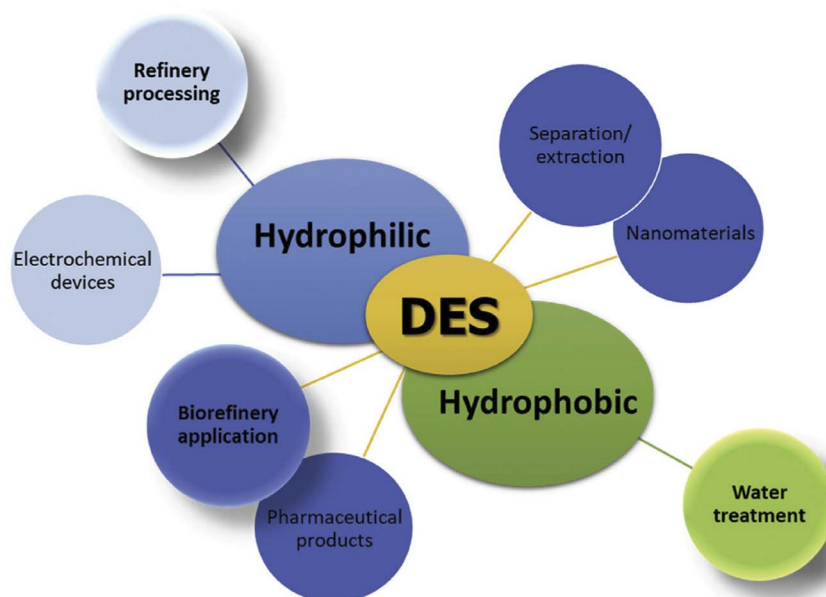
with the advantages of low toxicity, biodegradability, high thermal stability, non-flammability, no vapor pressure, and low production costs.<sup>18,26–28</sup>

The primary objective of this review is to examine a range of deep eutectic solvents (DESs) for their potential as innovative electrolytes in solar cells,<sup>29</sup> focusing on the synthesis and properties of DESs, with particular attention given to their physicochemical attributes that facilitate the conversion of CO<sub>2</sub> into value-added chemicals. The mechanism of these solar cells emulates the natural photosynthesis process and is termed “artificial photosynthesis”.<sup>30,31</sup> The review also outlines prospective avenues for future research within this area.

## 2. Deep eutectic solvents (DESs)

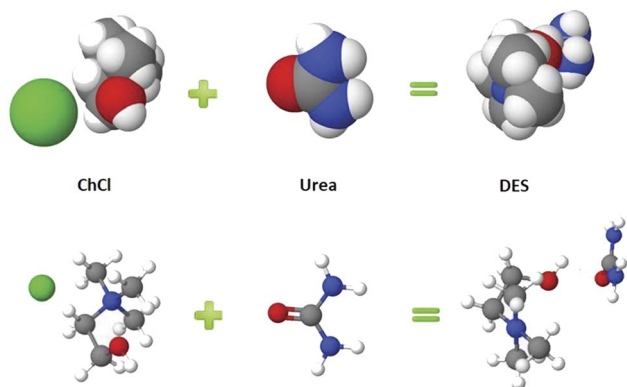
### 2.1. DESs as green solvents

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.<sup>32,33</sup> 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.<sup>34</sup> Deep eutectic solvents (DESs)<sup>35,36</sup> 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.<sup>37</sup> 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



Scheme 1 DES applications according to their individual hydrophilic and hydrophobic characteristics.<sup>19</sup>





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

point much lower than that of any of the individual components.<sup>38</sup> 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.<sup>39,40</sup>

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.<sup>41</sup> Some HBDs and HBAs used for the preparation of DESs introduced in this review are shown in Scheme 3.

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,  $\pi$ - $\pi$  bonding, or anion exchange).<sup>51</sup> 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 DESs.<sup>42</sup>

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 ( $\Delta T_f$ ) 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  $\Delta T_f$  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 water,<sup>43–47</sup> 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 them.<sup>48</sup> Scheme 5 shows the theoretical phase diagram for binary HBD and HBA mixtures, which illustrates how the mp or  $\Delta T_f$  of the DESs varies depending on the composition and ratio of the HBD and HBA.

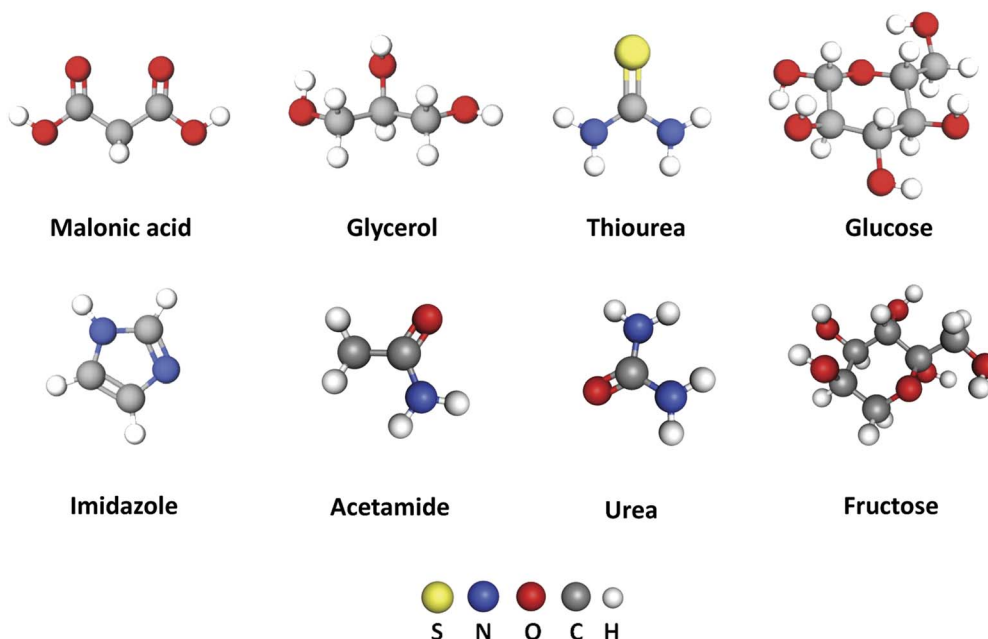
The DESs melting point influences the performance and stability of solar cells, as it affects the operating temperature range and the thermal degradation of the material.<sup>49</sup> The melting point of the DESs, as well as the polarity, viscosity, and density of the solvent, all have an impact on the solubility of  $\text{CO}_2$  in DESs. The  $\text{CO}_2$  solubility in a DES is inversely proportional to the melting point of the DESs. To obtain the correct melting point and solubility of  $\text{CO}_2$  in DESs for solar cell applications, it is important to select a suitable mix and proportion of HBD and HBA. The DESs 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 ( $\text{CaTiO}_3$ ). 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.<sup>49</sup> It is important to adjust the melting point and the heat treatment conditions of the DESs 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.

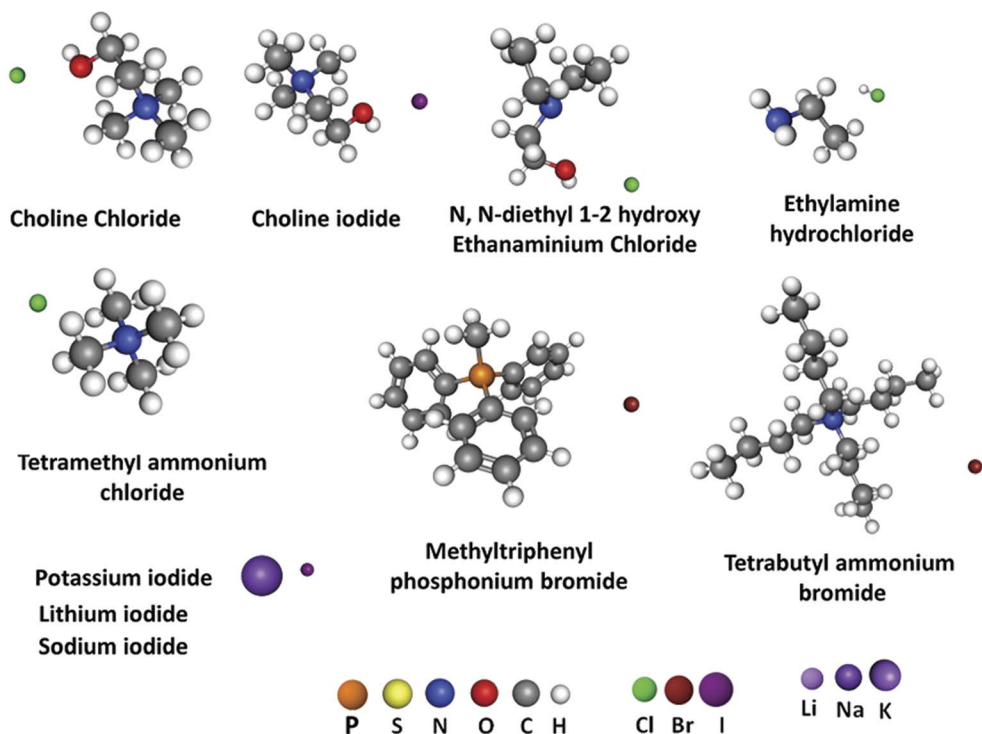
The viscosity of DESs depends on the type and ratio of the HBD and HBA components, as well as the interactions between them. The stronger the interactions, such as hydrogen bonds or van der Waals forces, the higher the viscosity of the DESs. The viscosity of DESs affects their performance and applications in various fields, such as solar cells,<sup>50</sup> electrochemistry,<sup>51</sup> catalysis,<sup>52</sup> and biotechnology.<sup>53</sup> For example, the viscosity of DESs affects the solubility of  $\text{CO}_2$  in them, which is an important factor for the conversion of solar energy and  $\text{CO}_2$  to useful products such as



## Hydrogen Bond Donors (HBDs)



## Hydrogen Bond Acceptors (HBAs)

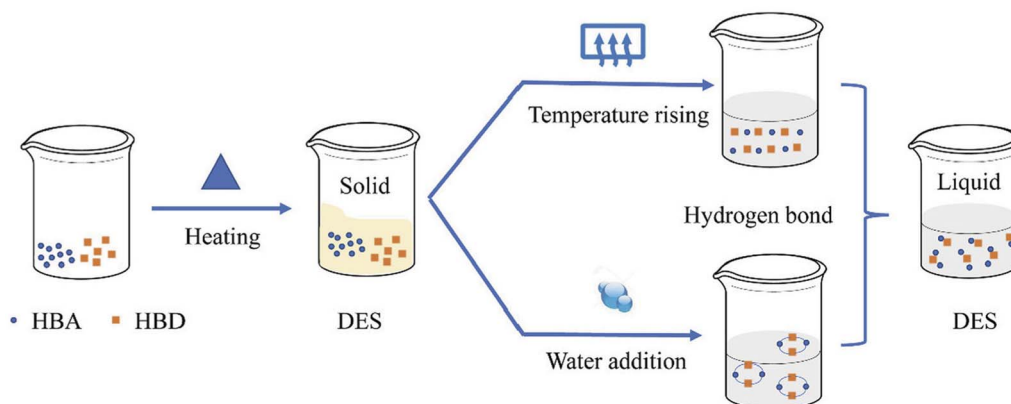


Scheme 3 Some hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) used in preparation of the DESs described in this review.

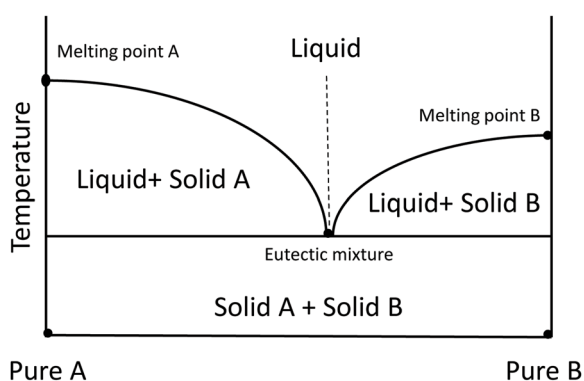
hydrocarbons. The solubility of  $\text{CO}_2$  in DESs decreases as the viscosity increases. Therefore, selecting the best mix and proportion of the HBD and HBA parts is important for achieving suitable  $\text{CO}_2$  solubility and viscosity in DESs for solar cell uses.

The temperature and the ionic species in the DESs electrolyte mixtures affect their viscosity, which is an indicator of the fluidity of the electrolyte. Heydari Dokohani *et al.*<sup>54</sup> used a DES based on choline chloride and ethylene glycol (ChCl-EG),





Scheme 4 The relationships between physicochemical properties, solvent performance, and applications of deep eutectic solvents.<sup>42</sup>



Scheme 5 Eutectic point in a two-component (HBA and HBD) phase diagram.<sup>39</sup>

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 DESs preparation enhanced the DSSC performance, but also increased the viscosity of the solution.

**2.2.3. Density.** The density ( $\rho$ ) 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 CO<sub>2</sub>, 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.<sup>55</sup> For example, at lower pressure, the ethylene glycol and CO<sub>2</sub> interaction dominates, while at a higher pressure, the chloride and CO<sub>2</sub> interaction is most important. Therefore, DESs offer the same advantages as the CO<sub>2</sub> absorbent in ionic liquids, while also exploiting a hydrogen bond donor.<sup>56</sup> 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.<sup>57</sup>

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.<sup>58</sup>

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 DESs-based electrolytes. For example, one study used a DES composed of choline chloride and urea (Reline)<sup>59</sup> as an electrolyte for carbon-based electrochemical capacitors. The study found that the specific capacitance increased from 100 to 157 F g<sup>-1</sup> at a 1 A g<sup>-1</sup> current load, by adding 1 wt% water to the DESs system, due to the decrease in viscosity and the increase in ionic conductivity.<sup>59</sup>

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 ( $V_{oc}$ ),<sup>60</sup> due to the different molecular structures and the ways that the DESs 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 carriers.<sup>61</sup>

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 DESs electrolyte exhibited higher power conversion efficiency, compared to DSSCs with a traditional liquid electrolyte, because the DES had higher conductivity and a lower recombination rate.<sup>62</sup> 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 DESs 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 interface.<sup>62</sup>

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 cm<sup>-1</sup>,<sup>63</sup> with the DESs 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 increases.<sup>64</sup>

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<sup>-1</sup> at ambient temperature).<sup>65</sup>

Hence, DESs are a good choice for electrochemical applications, including as electrolytes for solar cells, because they have low viscosity and high conductivity.<sup>63,66</sup>

**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.<sup>67,69</sup> 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 DESs 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.<sup>59</sup> 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<sub>2</sub>) 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<sub>2</sub>. The acidity of the DESs can affect the stability and corrosion of these materials by changing the chemical reactions that occur on their surfaces.<sup>68</sup> 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<sub>2</sub>, which reduces the catalytic activity of the counter electrode.<sup>69</sup> Higher acidity can also break down the ruthenium dye, which makes the photoanode less effective in absorbing light and injecting electrons.<sup>69</sup> Furthermore, higher acidity can cause hydrolysis of the ruthenium dye, which reduces light absorption and the electron injection efficiency of the photoanode.<sup>70</sup> 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.<sup>71,72</sup>

**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.<sup>72</sup> 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.<sup>73</sup> 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.<sup>74</sup> 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.<sup>16,47</sup> An aqueous choline chloride-based DES solution was utilized as an efficient electrolyte in DSSCs,<sup>60</sup> 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 CO<sub>2</sub>, 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.<sup>59,60,75,76</sup>

**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 CO<sub>2</sub>, 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.<sup>59,77,78</sup>

### 3. Preparation of DESs

#### 3.1. Selection of HBDs and HBAs

The main methods described in the literature for synthesis of DESs are based on stirring and heating, freeze drying, evaporation, and microwave-assisted synthesis.<sup>79</sup> The most popular method involves mixing and heating two or three components, until a homogeneous liquid is formed.<sup>80</sup> 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.<sup>43,46</sup> The DES type Cat<sup>+</sup>X<sup>-</sup> + zRZ, such as ChCl<sup>+</sup>urea, is especially popular due to its hydrophobicity and stability in aqueous mixtures.<sup>43</sup> The ultrasound-assisted and microwave-assisted DESs 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 solvents.<sup>81</sup> 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 DESs 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.<sup>79,86</sup> The introduction of ultrasound and microwave-assisted synthesis methods<sup>81</sup> 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 interactions.<sup>81</sup> 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 °C.<sup>81</sup>

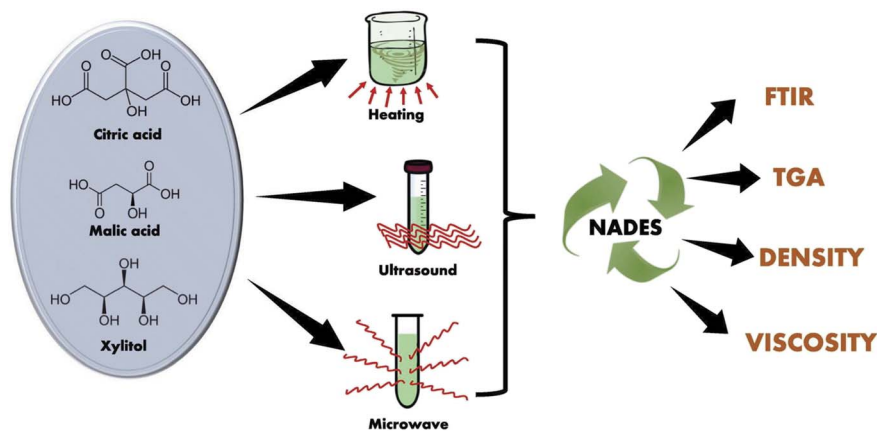
The Scheme 6 demonstrates that various synthesis methods can yield NADES with consistent properties, despite differences in efficiency and equipment requirements. Researchers can choose the most suitable method based on their specific needs and constraints, and all synthesis methods yield NADES with similar physicochemical characteristics.<sup>81</sup>

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 agents,<sup>82–84</sup> 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





Scheme 6 The synthesis of NADES using different methods.<sup>81</sup>

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 CO<sub>2</sub>, low surface tension, and high conductivity.<sup>59,85</sup>

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,<sup>86,87</sup> 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 parameters.<sup>86</sup>

### 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.<sup>59</sup> 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<sup>-1</sup> at a 1 A g<sup>-1</sup> 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.<sup>88</sup> 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 CO<sub>2</sub> in DESs

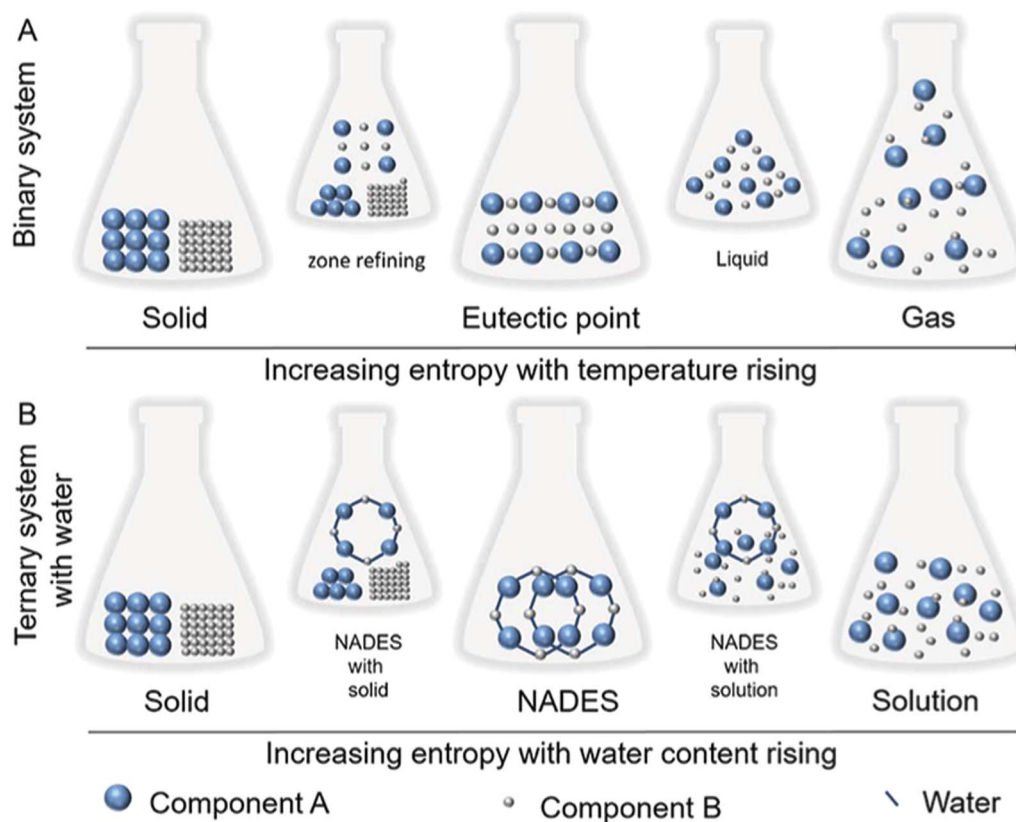
The solubility of CO<sub>2</sub> in DESs is an important factor for using them as electrolytes in solar cells, as it affects the conductivity, stability, and performance of the devices. CO<sub>2</sub> is a greenhouse gas that solar cells can capture and utilize to produce electricity and reduce emissions. However, the solubility of CO<sub>2</sub> 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 CO<sub>2</sub> in 109 different DESs, covering a wide range of temperatures and pressures.<sup>89</sup> It was found that the PC-SAFT model could provide accurate and reliable predictions of CO<sub>2</sub> 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







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

point, high solubility, and high conductivity, which are desirable properties for solar cell electrolytes. They can also capture and utilize CO<sub>2</sub>, 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 DSSCs performance.<sup>59</sup> 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, DESs<sup>60</sup> 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. CO<sub>2</sub> has low solubility in water (0.033 M) under ambient conditions,<sup>90</sup> which limits the efficiency of its adsorption and conversion in solar cells. A common technique for CO<sub>2</sub> capture is using amine solvents, which have high selectivity and capacity, but also have drawbacks such as high corrosiveness<sup>91</sup> and high energy consumption,<sup>92</sup> which hinders their use in solar cells.<sup>93,94</sup>

DESs have attracted attention in both experimental and theoretical studies, due to their ability to efficiently capture CO<sub>2</sub>. In particular, a combination of ethanolamine hydrochloride (HBA) and tetraethylenepentamine (HBD) in a ratio of 1 : 9, referred to as EAHC-TEPA, showed remarkable CO<sub>2</sub> solubility, among several DESs investigated.<sup>95</sup> Haider and Kumar<sup>96</sup> developed amine-based DESs with bulky structures that exhibited superior CO<sub>2</sub> uptake, while maintaining minimal CH<sub>4</sub> absorption, demonstrating a pronounced preference for CO<sub>2</sub>.

Studies have explored the integration of CO<sub>2</sub> sequestration and transformation using amine-based solvents that can absorb CO<sub>2</sub> and serve as electrolytes for electrochemical conversion. Pérez-Gallent *et al.*<sup>97</sup> 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] ([MEAHC][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 [MEAHC][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 CO<sub>2</sub> reduction efficiency, due to its favorable CO<sub>2</sub> solubility.<sup>98</sup> In a similar vein, [MEAHC][MDEA], as a novel aqueous amine-based deep eutectic solvent, was formulated as an electrolyte for the reduction of CO<sub>2</sub> 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 [MEAHC][MEA] by 33%.<sup>99</sup>

Building on these studies, other work developed a DES by combining choline chloride and ethylene glycol, for use as an electrolyte.<sup>100</sup> This new formulation replaced dimethylformamide (DMF) and contributed to advancements in DSSCs technology, showing improved efficiency in the electrochemical reduction of CO<sub>2</sub>, attributed to enhanced CO<sub>2</sub> 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 CO<sub>2</sub> solubility.

In addition, imidazole and its derivatives have long been recognized as potent components in ionic liquids (ILs) and DESs for enhancing CO<sub>2</sub> solubility.<sup>101,102</sup> 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 CO<sub>2</sub>.<sup>103</sup> Boualavong and Gorski<sup>104</sup> employed a chemical reaction equilibrium model to explore how variations in the substituent groups of imidazole affected CO<sub>2</sub> capture efficiency and energy requirements. The authors proposed a method to reduce the energy consumption of electrochemical capture technologies by doubling the number of CO<sub>2</sub> 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.

As shown in Table 1, the solubility of CO<sub>2</sub> in DESs is influenced by both temperature and pressure. Generally, the solubility of a gas such as CO<sub>2</sub> decreases with increase in temperature and decrease in pressure.<sup>120</sup> 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 CO<sub>2</sub>, 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.<sup>121</sup> 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.<sup>60</sup>

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.<sup>60</sup> In particular, the CO<sub>2</sub> 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.

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 <sup>-1</sup> )	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



## 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  $\text{TiO}_2$  layer.

A DSSC (as shown in Scheme 8) classically consists of the following components:<sup>78</sup> (1) a photo-sensitized anode, usually made of a semiconductor material such as titanium dioxide ( $\text{TiO}_2$ ), 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 ( $\text{I}^-$ ) and tri-iodide ( $\text{I}_3^-$ ) 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 ( $\text{I}^-$ ) acts as a charge carrier, while the triiodide ion ( $\text{I}_3^-$ ) helps the oxidized dye molecules to regenerate, completing the electrical circuit of the cell.<sup>122</sup> 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.

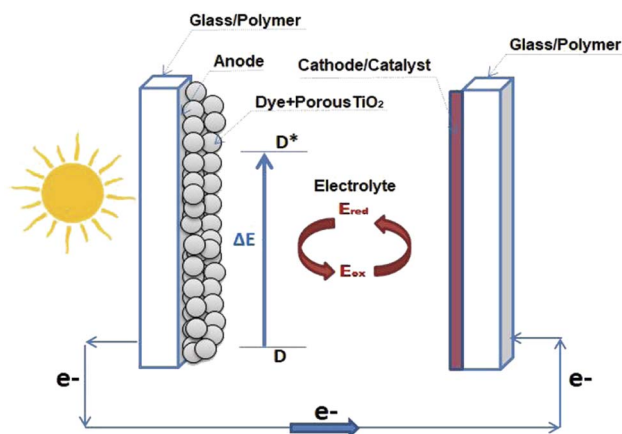
The fabrication of DSSCs is mostly performed according to a well-established protocol,<sup>123</sup> to prevent metal contamination. The glass or Teflon containers are firstly cleaned with ethanol (EtOH) and a 10% hydrochloric acid (HCl) solution. Throughout

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- $\text{O}_3$  for 18 min. The UV- $\text{O}_3$  method, which combines ultraviolet (UV) light and ozone ( $\text{O}_3$ ) 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  $\text{TiCl}_4$  solution, at 70 °C, followed by rinsing. A transparent layer of  $\text{TiO}_2$  (determined by measurement of an area of 0.20  $\text{cm}^2$ ) is applied onto the substrate using a screen-printing technique, with a 20 nm particle size paste. After applying the  $\text{TiO}_2$  layer, the material is submitted a series of drying and heat treatments at progressively higher temperatures. After sintering, the layer is treated again with  $\text{TiCl}_4$  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  $\mu\text{L}$   $\text{H}_2\text{PtCl}_6$  solution in EtOH is deposited onto the plate, and then heat-treated at 500 °C for 30 min. At the time a hot-melt ion-omer resin spacer is inserted between the dye-coated  $\text{TiO}_2$  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.

A survey of commonly used photocatalyst substances<sup>124,125</sup> 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)  $\text{TiO}_2$ , 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;<sup>123</sup> (2) absorption of fluorescent light, in addition to sunlight, which is beneficial for indoor applications;<sup>123</sup> (3) flexibility in the design and application of the solar cells, as a result of the thin-film nature of DSSCs;<sup>126</sup> (4) good performance under conditions of low light, making them useful in less sunny climates;<sup>127</sup> (5) use of eco-friendly materials in the construction of DSSCs, contributing to a greener production process;<sup>128</sup> (6) versatility for use in a wide range of environments and ability to be integrated into various solar products.<sup>128</sup>

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



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



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.

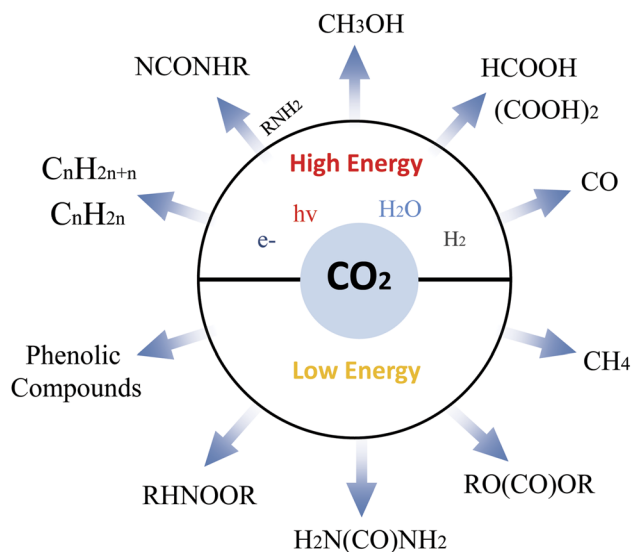
#### 4.2. Application of DSSCs in CO<sub>2</sub> conversion

DSSCs have recognized potential in various applications, including the conversion of CO<sub>2</sub> to obtain useful products.<sup>129</sup> The literature lacks specific details on the application of DSSCs in CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> into compounds such as formic acid, methanol, or other carbon-based products. This process not only helps in mitigating CO<sub>2</sub> emissions, but also provides a sustainable pathway for chemical synthesis.

This process essentially mimics photosynthesis,<sup>78</sup> using solar energy to convert CO<sub>2</sub> into organic compounds. The efficiency and selectivity of the CO<sub>2</sub> 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 CO<sub>2</sub> 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<sub>2</sub> into high-value products such as HCOOH, CO, CH<sub>2</sub>O, CH<sub>3</sub>OH, and CH<sub>4</sub> is of paramount importance.<sup>130</sup> 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 products from CO<sub>2</sub>.

Any chemical transformation of CO<sub>2</sub> requires energy, but there are distinct processes with varying energy requirements. Low-energy processes incorporate the entire CO<sub>2</sub> molecule into an organic or inorganic substrate. For instance, consider the series: CO<sub>2</sub> → HCOOH (formic acid) → CO → CH<sub>2</sub>O (formaldehyde) → CH<sub>3</sub>OH (methanol) → CH<sub>4</sub> (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<sub>2</sub> to -4 in methane (CH<sub>4</sub>). These processes have the potential to produce fuel.<sup>130</sup> If we focus solely



Scheme 9 Production of chemicals from CO<sub>2</sub> at different energy level.

on chemical synthesis, we'll recycle limited amounts of CO<sub>2</sub>. However, if we prioritize fuel we could potentially recycle larger volumes of CO<sub>2</sub>. 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<sub>2</sub> conversion.<sup>130</sup>

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.<sup>134,135</sup> To address these issues, the adoption of green and efficient methods is crucial for the production of diverse carboxylic acids by CO<sub>2</sub> 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 CO<sub>2</sub> conversion in DSSCs

In DSSCs, the conversion of CO<sub>2</sub> is facilitated by a photoelectrochemical process, with the DSSC acting as a catalyst for the transformation of CO<sub>2</sub> 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 TiO<sub>2</sub>), 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 CO<sub>2</sub> 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.<sup>123</sup>

Enhancing the efficiency of solar cells is crucial for optimizing the conversion of solar energy and CO<sub>2</sub> into valuable products such as HCOOH, CO, CH<sub>2</sub>O, CH<sub>3</sub>OH, and CH<sub>4</sub>.<sup>130</sup> Among these products, carboxylic acids, especially formic acid (HCOOH),<sup>133</sup> 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.<sup>131,132</sup> To address these issues, there is an urgent need for sustainable and effective techniques to generate a range of carboxylic acids by CO<sub>2</sub> reduction. Honda *et al.* accomplished the photocatalytic reduction of CO<sub>2</sub> to hydrocarbons in 1970.<sup>134</sup> Subsequent research has continued to advance the field of photocatalytic CO<sub>2</sub> reduction.<sup>135–137</sup>

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<sub>x</sub>) 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 processes.<sup>138</sup>

The process of converting CO<sub>2</sub> into carboxylic acids by photocatalysis, shown in Scheme 10, begins when the catalysts,

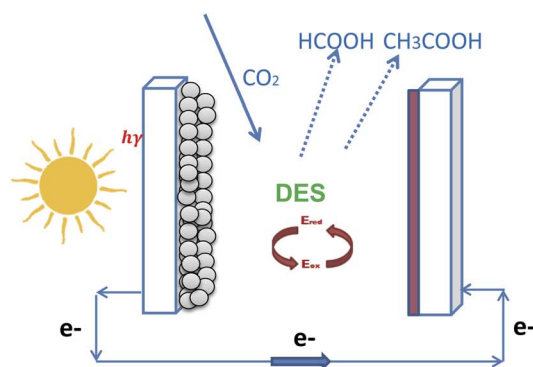
typically semiconductor materials, are subjected to light irradiation. This exposure causes electrons within the semiconductor to become excited, leaving behind positively charged vacancies known as holes. These photogenerated electron-hole pairs are crucial to the process, as they are separated and directed towards the active sites of the catalyst.

Once at the surface, the photogenerated electrons assist in the reduction of CO<sub>2</sub>, transforming it into various useful fuels (CO, CH<sub>4</sub>, CH<sub>3</sub>OH, and others). The presence of water (H<sub>2</sub>O) 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<sup>-</sup>), while the production of methanol (CH<sub>3</sub>OH) necessitates six electrons (6e<sup>-</sup>), and methane (CH<sub>4</sub>) production requires eight electrons (8e<sup>-</sup>).<sup>139,140</sup>

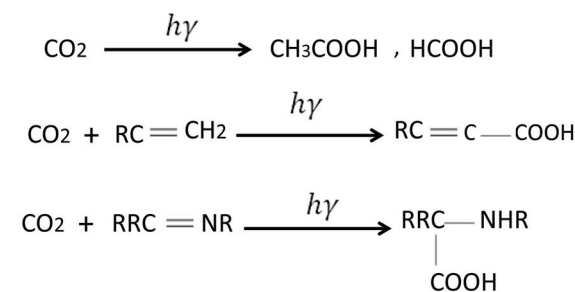
This photo-electrocatalytic process is a promising green technology for CO<sub>2</sub> reduction, as it utilizes sunlight, a renewable energy source, and can potentially lead to the creation of valuable chemicals and fuels. The efficiency and selectivity of the process can be influenced by the choice 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.<sup>141</sup>

#### 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*<sub>oc</sub>) and the short-circuit current (*I*<sub>sc</sub>), 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



Scheme 10 Different carboxylic acid reaction paths in solar cells.<sup>130</sup>



photovoltaic devices, aligning with the goals of producing low-cost and eco-friendly materials for large-scale production.<sup>60,141</sup>

As discussed above, DSSCs consist of an anode made of a thin titanium dioxide (TiO<sub>2</sub>) layer that is sensitized by a suitable dye.<sup>142,143</sup> 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.<sup>25,144,145</sup> 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<sub>2</sub> 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<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple is the one most used in DSSCs, although other redox couples such as CO<sup>2+</sup>/CO<sup>3+</sup> or Cu<sup>+</sup>/Cu<sup>2+</sup> have also been explored for their potential benefits.<sup>146,147</sup>

#### 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*<sub>sc</sub>), the open-circuit voltage (*V*<sub>oc</sub>), and the fill factor (FF). The *J*<sub>sc</sub> value represents the peak current output of the cell, observed at zero voltage, while the *V*<sub>oc</sub> 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*<sub>out</sub>) to the theoretical maximum power (*J*<sub>sc</sub> × *V*<sub>oc</sub>). PCE is defined as the ratio of the power output (*P*<sub>out</sub>) to the power input (*P*<sub>in</sub>), with the output power density being the product of *J*<sub>sc</sub>, *V*<sub>oc</sub>, and FF. Therefore, PCE can be expressed by the following equation:

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

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 nano-structured materials (such as TiO<sub>2</sub>) 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.<sup>78,148,149</sup>

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.<sup>150</sup> 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.<sup>151</sup>

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, TiO<sub>2</sub>) 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 properties.<sup>150</sup> Additional research investigates potential sensitizers for DSSCs, such as nanocomposites of graphene quantum dot hybrids and their Cu-metallated macrocycles.<sup>151</sup> Besides, other study examined the structural and electrical characteristics, as well as the absorption spectra, of supramolecular triads consisting of fullerene and porphyrine in DSSCs.<sup>152</sup> 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-ZnP double



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.<sup>152</sup>

Optimizing the band gap, maximizing  $J_{sc}$ , and achieving an appropriate  $V_{oc}$  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.<sup>152,153</sup> 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 (TiO<sub>2</sub>). 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: optimizing DSSC performance, ensuring effective light absorption, and enhancing the overall efficiency of these solar cells. (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.<sup>152</sup>

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.<sup>153</sup> 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<sub>2</sub>. Maximizing LHE involves minimizing charge recombination and enhancing light trapping within the DSSCs.<sup>152</sup> In order to enhance LHE, it is necessary to fine-tune the sensitizing

properties, developing sensitizers with ideal HOMO–LUMO energy levels and absorption characteristics.<sup>153</sup> In addition, the integration of nanostructures such as nanowires and nanoparticles can be employed to improve the capture and absorption of light.<sup>154</sup> 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 cell.<sup>155</sup>

The calculated LHE for triad complexes using ZINDO/S method reported,<sup>152</sup> 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 complexes<sup>152</sup> 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  $\pi$  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.<sup>156</sup>

ILs/DESSs have been used as electrolytes in DSSCs since 2009,<sup>17</sup> 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<sup>157,158</sup> 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.

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 ( $\eta$ ). 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.



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

DESs	Iodide source	Dye/other adsorbent	TiO <sub>2</sub> thickness	Dilution	Remark	Advantages	Ref.
Choline chloride + glycerol	PMII and G.Cl 13 : 7 v/v	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 EmimI 0.3 M EmimI 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	Coupled redox mediator (e.g., I <sup>-</sup> /I <sub>3</sub> <sup>-</sup> )	N719	T	Up to 40% 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 <sup>-</sup> /I <sub>3</sub> <sup>-</sup> )	N719	T	No diluting agent	Improved open circuit voltage (V <sub>oc</sub> )	Simple preparation, biodegradable, low-cost	60
Choline chloride + ethylene glycol	Coupled redox mediator (e.g., I <sup>-</sup> /I <sub>3</sub> <sup>-</sup> )	N719	T	No diluting agent	Increase in short circuit current (I <sub>sc</sub> )	Nontoxic, available materials, comparative conversion efficiency	60
Betaine + glycerol	Coupled redox mediator (e.g., I <sup>-</sup> /I <sub>3</sub> <sup>-</sup> )	N719	T	No diluting agent	Comparable efficiency to conventional electrolytes	Renewable, biodegradable, non-corrosive	60
Choline chloride + phenol	Redox mediator (e.g., I <sup>-</sup> /I <sub>3</sub> <sup>-</sup> )	N719	T	No diluting agent	Improved V <sub>oc</sub> values by 10–40 mV, higher short circuit current (I <sub>sc</sub> ) not observed with 4-TBP	Eco-friendly, low cost, simple synthesis, used new efficient and eco-friendly additives	77

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 ( $\lambda$ ). 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 ( $\lambda$ ).<sup>17,161</sup>

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<sub>2</sub>; 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.*,<sup>18</sup> 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<sub>2</sub> 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.*,<sup>17</sup> 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.*<sup>16</sup> 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 a deep eutectic solvent (DES) with acetonitrile (ACN) showed the most promising results, among these studies.<sup>25,162,163</sup> 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-*t*BP, and ACN to further enhance the performance of DSSCs.<sup>164,168</sup> 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 efficiency.<sup>164-166</sup>

One area of focus was the behavior of a 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<sup>-1</sup> 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<sup>-1</sup>) was reported to provide an effective electrolyte solvent for DSSCs.<sup>16</sup> 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<sup>161</sup> 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<sup>+</sup> to K<sup>+</sup>. 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<sub>2</sub> 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<sup>+</sup> to K<sup>+</sup>. 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<sub>2</sub> and Pt electrodes.<sup>161</sup>

#### 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<sub>2</sub>-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 (DESs) in environmentally friendly DSSCs, researchers continue to explore DES properties and address challenges to enhance their performance.<sup>167,168</sup>

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<sub>2</sub>) to accommodate DESs phase changes. (4) Applying thin coatings (e.g., graphene, polymers) to improve DESs adhesion and stability. (5) Modifying TiO<sub>2</sub> electrodes with hydrophilic or DES-compatible functional groups to enhance wetting behavior. (6) Optimizing ion migration pathways within the cell to minimize DESs viscosity effects. (7) Investigating DESs recyclability and exploring methods for reusing or regenerating DESs. (8) 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 DESs with polymers to create hybrid materials. These blends could offer improved mechanical strength, thermal stability, and ion transport properties, or combine graphene into DESs to enhance electrical conductivity and provide a conductive network within the electrolyte. (2) Developing DESs that responds to environmental cues (e.g., temperature, light) by altering its properties. This adaptability could enhance DSSCs performance under varying conditions. (3) Investigating DESs 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 CO<sub>2</sub> into added-value products. (5) Developing efficient methods to recycle DESs 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 literature showed that the ability of CO<sub>2</sub> to dissolve in DESs can greatly improve the capacity of solar cells to convert CO<sub>2</sub> 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 CO<sub>2</sub> solubility. The addition of potassium iodide (KI) to DESs 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 CO<sub>2</sub> solubility in DESs for the capture and utilization of CO<sub>2</sub> by solar cells. Certain DESs demonstrate a high capacity and selectivity for CO<sub>2</sub> 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.

## 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
$I^-/I_3^-$	Iodide/triiodide
TiO <sub>2</sub>	Titanium dioxide
NADES	Natural Deep Eutectic Solvents
ECs	Electrochemical Capacitors
F.E.	Faradaic Efficiencies
MEAHC1	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
$E_g$	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]	1-Butyl-3-methylimidazolium
[tf2N]	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

## Author contributions

Khatereh A. Pishro: formal analysis, investigation, writing – review & editing, original draft. Mario Henrique Gonzalez: supervision, conceptualization, project administration, resources, writing – review & editing.

## Conflicts of interest

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