

# Eco-friendly sugar-based natural deep eutectic solvents as effective electrolyte solutions for dye-sensitized solar cells

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Dedicated to Dr. Maurizio Peruzzini on the occasion of his 65<sup>th</sup> birthday, and his retirement from the National Research Council of Italy.

**Abstract:** Dye-sensitized solar cells containing sugar-based Natural Deep Eutectic Solvents (NADESs) as active electrolyte solvents have been studied in their photovoltaic (PV) properties, including main PV characteristics, IPCE, and EIS. Five monosaccharides were selected as NADES H-bond donors and investigated with a phenothiazine-based sensitizer carrying a glucose functionality and a glucose-based co-adsorbent (glucuronic acid) to explore directional intermolecular interactions and improve the PV performance. The highest power conversion efficiencies were recorded for cells containing the glucose-based sensitizer in the presence of glucuronic acid in the sugar-based NADES. When one of these components was omitted, performances were lower suggesting that the best response came from an interplay between the sugar-based units. Not only has the unprecedented use of a NADES as a fully natural and bio-renewable DSSC medium been presented, but for the first time an active role of the electrolyte solvent has been reported and exploited to increase the performance of the solar device.

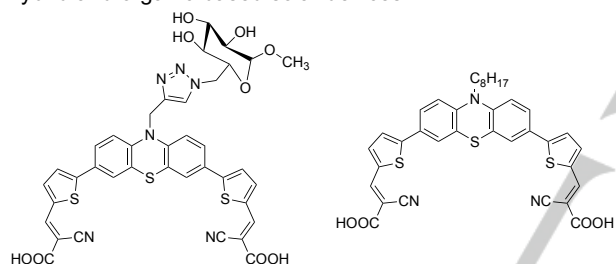
## Introduction

In the present time of global pollution and global warming, renewable energies are gaining increasing relevance.<sup>[1]</sup> Among all the different technologies today available for producing electricity from solar energy, dye-sensitized solar cells (DSSCs) represent a powerful approach since their very first appearance in the literature by Gratzel and O' Regan in 1991.<sup>[2]</sup> One of the advantages of DSSCs lies in their modularity, so that every single part of the cell can be separately modified and optimized.<sup>[3]</sup> This emphasis on environmental issues has, in turn, led to a profound paradigm shift also in energy technology. Indeed, many efforts have been made (a) to synthesize dyes with enhanced light absorption,<sup>[4]</sup> (b) to find cheaper and more efficient redox couples for the electrolyte solution,<sup>[5]</sup> and (c) lately also to explore more sustainable solvents for the liquid electrolyte solution, such as water.<sup>[6]</sup> In compliance with the philosophy of green chemistry, one of its purposes being to curb the production of pollutants,<sup>[7]</sup> our groups have recently reported a number of DSSC devices based on either hydrophilic or hydrophobic Deep Eutectic

Solvents (DESSs).<sup>[8]</sup> DESSs are binary or ternary mixtures comprising at least one hydrogen bond donor and at least one hydrogen bond acceptor, which are strongly associated with each other via hydrogen bond interactions, so as to form an eutectic mixture with a melting point much lower than those of either individual components and that of an ideal liquid mixture. DESSs are cheap neoteric solvents with a low ecological footprint and represent a sustainable alternative to toxic and volatile organic compounds (VOCs), which are still used in liquid-electrolyte DSSCs (e.g., acetonitrile), because of their negligible vapour pressure, essential nontoxicity and biodegradability, and easy recyclability.<sup>[9]</sup>

In our previous works,<sup>[8]</sup> we have focused special attention in providing a first proof of concept of the successful exploitation of DESSs as *passive* electrolyte solvents in DSSCs. In this work, we plan to investigate the potential *active* involvement of DES media in the solar energy production process of DSSCs by means of directional and specific cooperative interactions between the photosensitizer, which is known to play a key role in the whole process, and the so-called "Natural Deep Eutectic Solvents" (NADESs). NADESs are thought to be the missing link in understanding cellular metabolism and physiology<sup>[10]</sup> as their typical constituents are primary metabolites (e.g., amino acids, carbohydrates, organic acids) which are usually present at high concentrations in cells. In order to do this, we have prepared some sugar-based NADESs to be tested in combination with a proper sugar-based photosensitizer that some of us have already successfully tested in photocatalytic hydrogen generation.<sup>[11]</sup> By investigating these processes, we have experimentally and computationally demonstrated that the sugar-based dye is able to induce strong and directional intermolecular interactions with the other key device components in order to exploit the higher supramolecular architecture in the enhanced hydrogen generation. Also, in DSSCs intermolecular interactions among the different device components are expected to play a strategic role in the overall cell performance because of the importance of the interfacial effects involving the electrolyte medium. In particular, we expect that a fruitful cooperation between a sugar-based dye, a sugar-based co-adsorbent (namely, glucuronic acid) and a

sugar-based NADES may take place eventually affording to improved cell power conversion efficiencies (PCE) compared to conventional device components without the sugar functionality. As a representative dye, we have selected a donor-acceptor molecule where the donor core is the phenothiazine core bearing, through the phenothiazine nitrogen atom, a glucose-based functionality (**PTZ-Glu**, Figure 1). We have already reported its use as a photosensitizer in the photocatalytic hydrogen generation in combination with glucuronic acid.<sup>[11a]</sup> These experiments were focused on the exploitation of the possible interaction via hydrogen bonding to improve the device efficiency when operating in aqueous media (i.e. 10% triethanolamine in water at pH 7). In particular, we have found that, when **PTZ-Glu** is covalently attached onto TiO<sub>2</sub>, hydrogen production is improved due to the formation of directional intermolecular interactions with glucuronic acids as well as to a highly hydrophilic character of the semiconductor surface.<sup>[11b]</sup> The proposed interaction between **PTZ-Glu** and glucuronic acid has been investigated with computational methods to support this hypothesis. These peculiar characteristics may be properly exploited in combination with a suitable water-diluted NADES,<sup>[12]</sup> an affinity that is likely further enhanced by the presence of the sugar functionalities. Aside from the aforementioned works,<sup>[8]</sup> very few examples of DES-based DSSCs have been reported so far in the literature.<sup>[13]</sup> Thus, this work represents an innovative research topic in the large field of hybrid and organic-based solar devices.



**Figure 1.** Chemical structure of the tested dyes: **PTZ-Glu** (left) and **PTZ-Th** (right).

## Results and Discussion

In order to properly investigate the active role of sugar-based NADESs in DSSCs containing a sugar-derivative as a photosensitizer, we have decided to explore a set of 5 different NADESs containing 5 different monosaccharides, including the most abundant monosaccharide D-glucose. In particular, we have selected the following carbohydrates as H-bond donors in

combination with different amounts of choline chloride (ChCl), and the corresponding mixtures have been diluted with water in order to reach a viscosity compatible with device preparation: D-glucose, D-sorbitol, D-fructose, and D-mannose (Table 1) in the presence of I<sup>-</sup>/I<sub>3</sub><sup>-</sup> as a redox mediator. As a control experiment, we have used as a reference the prototypical ChCl/glycerol (Gly) (1:2 mol/mol) eutectic mixture (diluted with 40% w/w water, GLYCD-DES), which has previously been investigated in DSSC studies with conventional dyes.<sup>[8b]</sup>

**Table 1.** Sugar-based NADES composition.

NADES sample	Sugar	Sugar:ChCl ratio	Water wt%
GLU-NADES	Glucose	1:2	30
SORB-NADES	Sorbitol	1:1	30
FRU-NADES	Fructose	2:1	20
MAN-NADES	Mannose	2:5	20

As a DSSC photosensitizer, we have used the glucose phenothiazine di-branched derivative **PTZ-Glu**. For comparison, we have also investigated cells containing the corresponding di-branched sensitizer where the terminal sugar functionality has been replaced by a C<sub>8</sub>-alkyl substituent on the phenothiazine nitrogen atom (**PTZ-Th**), which is not expected to induce directional intermolecular forces with the sugar-based NADESs.<sup>[14]</sup> The structure of the two dyes are shown in Figure 1. Finally, we have tested as a co-adsorbent both the commonly used chenodeoxycholic acid (**CDCA**), which is not optimised for strong interactions with sugar derivatives, and glucuronic acid (**GA**), for which specific intercomponent interactions are expected.<sup>[15]</sup>

As a first test, we have compared the performance of different sugar-based NADESs with both dyes, with no co-adsorbent added in order to only investigate the interaction between NADES and the sensitizer. The results from the best performing cells are collected in Table 2 and graphically depicted in Figure S1. The average values of five independent different cells for each sample and their standard deviation are listed in Table S1. From these data, we conclude that there is no significant difference when using the two dyes. Actually, in most cases, the alkyl derivative **PTZ-Th** has been found to provide higher PCE, either due to higher photocurrent  $J_{sc}$  or to higher photovoltage  $V_{oc}$ . Thus, without the co-adsorbent, no particular interface interactions involving the NADES medium take place.

**Table 2.** Photovoltaic parameters of DSSC with **PTZ-Glu** vs **PTZ-Th** dyes.

PTZ-Glu sensitised cells				PTZ-Th sensitised cells				
$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	<i>FF</i>	<i>PCE</i> (%)	NADES	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	<i>FF</i>	<i>PCE</i> (%)
3.3	509	0.50	0.8	<b>GLY-NADES</b>	2.7	512	0.47	0.7
2.2	549	0.72	0.9	<b>GLU-NADES</b>	1.9	557	0.77	0.8
1.1	532	0.68	0.4	<b>SORB-NADES</b>	1.2	546	0.73	0.5
0.96	488	0.47	0.2	<b>FRU-NADES</b>	0.7	549	0.75	0.3
1.6	488	0.52	0.4	<b>MAN-NADES</b>	2.2	546	0.70	0.8

In the subsequent step, we have introduced the effect of adding either the conventional co-adsorbent **CDCA** or the sugar-derivative **GA**. This step is critical since we now expect a different behaviour in analogy with our previous photocatalytic hydrogen generation experiments where the interaction between the sugar-based dye and the co-adsorbent proved to play a strategic

role.<sup>[11a]</sup> We have used an optimal 1:10 dye:co-adsorbent ratio in order to have a direct comparison with previously reported data.<sup>[8]</sup> The best results are collected in Table 3 and depicted in Figure S2. The average values of five independent different cells for each sample and their standard deviation are listed in Table S2

**Table 3.** Photovoltaic parameters of DSSC with **PTZ-Glu** and **GA** as a co-adsorbent vs **PTZ-Th** and **CDCA** as a co-adsorbent.

PTZ-Glu:GA 1:10				NADES	PTZ-Th:CDCA 1:10			
$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	FF	PCE (%)		$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	FF	PCE (%)
4.3	483	0.57	1.2	<b>GLYC-NADES</b>	2.6	555	0.56	0.8
4.0	527	0.64	1.4	<b>GLU-NADES</b>	1.8	565	0.79	0.8
3.6	502	0.64	1.2	<b>SORB-NADES</b>	0.9	556	0.74	0.4
3.4	523	0.68	1.2	<b>FRU-NADES</b>	1.1	543	0.77	0.5
1.8	546	0.62	0.6	<b>MAN-NADES</b>	2.1	552	0.68	0.8

It is now evident that the overall picture has drastically changed compared to the previous set of experiments. With only one exception, where a similar behaviour was recorded, for all sugar-based NADESs the pair **PTZ-Glu:GA** has always afforded a significantly improved (up to 4-fold) PCE compared to the pair **PTZ-Th:CDCA**. This improvement is mostly associated to a photocurrent enhancement, whereas the photovoltage and fill factor (FF) were only marginally or randomly affected. The highest PCE (1.4%) has been recorded for **PTZ-Glu:GA** in **GLU-NADES**, with an improvement of nearly 100% compared to the conventional dye/co-adsorbent (0.8%). In particular, the measured photocurrent for **PTZ-Glu:GA** was more than twice higher than that using **PTZ-Th:CDCA**. The highest PCE improvement (4-fold) has been recorded for **SORB-NADES**, as a result of the ~ 4-fold increase in cell photocurrent. However, from data of Table 3, we cannot rule out that the role of the glucose-based NADES is subordinate with respect to the cooperative enhancement induced by the use of the pair **PTZ-Glu:GA**, as we have ascertained in our previous photocatalytic hydrogen generation experiments.<sup>[11a]</sup> In that work, we have demonstrated that directional intermolecular dye-co-adsorbent

interactions take place on the semiconductor surface and that the induced supramolecular order is at the origin of the enhanced device performance. Here, we can expect a similar supramolecular arrangement of the TiO<sub>2</sub> surface, that likely suppresses detrimental self-quenching phenomena of the photoexcited states. This may explain the superior performances detected in our system.

On the other hand, by simply adding the co-adsorbent **CDCA** to **PTZ-Th** cells, PCE was not improved. This was expected since it had already been demonstrated that the butterfly structure of phenothiazine derivatives prevent aggregation among molecules when absorbed onto a substrate, thus making useless the presence of a co-adsorbent to prevent self-quenching.<sup>[16]</sup> In the third set of experiments, we have recombined the dye/co-adsorbent pairs in the presence of different NADESs. That is, we have tested **PTZ-Glu** in combination with **CDCA**, and **PTZ-Th** in combination with **GA** to check if the presence of **GA** itself could be enough to boost cell performance. The data from the best performing devices are collected in Table 4 and Figure S3. The average values of five independent different cells for each sample and their standard deviation are listed in Table S3.

**Table 4.** Co-adsorbent cross-test: *J/V* characteristics of DSSC with **PTZ-Th** and **GA** as a co-adsorbent vs **PTZ-Glu** and **CDCA** as a co-adsorbent.

PTZ-Th + GA 1:10				NADES	PTZ-Glu + CDCA 1:10			
$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	FF	PCE (%)		$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	FF	PCE (%)
2.2	475	0.54	0.6	<b>GLYC-NADES</b>	3.7	524	0.59	1.2
1.6	457	0.63	0.5	<b>GLU-NADES</b>	2.1	544	0.72	0.8
1.3	505	0.56	0.4	<b>SORB-NADES</b>	1.3	530	0.72	0.5
0.46	511	0.67	0.2	<b>FRU-NADES</b>	0.76	566	0.73	0.3
1.3	482	0.65	0.4	<b>MAN-NADES</b>	2.0	554	0.73	0.8

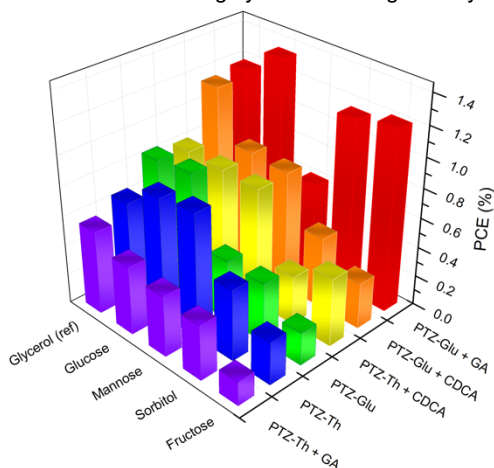
From these data, it is apparent that the presence of **GA** in combination with **PTZ-Th** is not sufficient to improve PCE. Device performances of **PTZ-Th** sensitized cells are similar either when using **CDCA** or **GA** as a co-adsorbent. Analogously, the

efficiencies of **PTZ-Glu:CDCA**-based cells are lower than those recorded in the previous experiment, when **GA** was used as a co-adsorbent.

We can therefore conclude that none of the tested components can justify the best results alone, but it is collectively the interplay between the sugar-based sensitizer, the co-adsorbent, and the NADES responsible for the highest device performance.

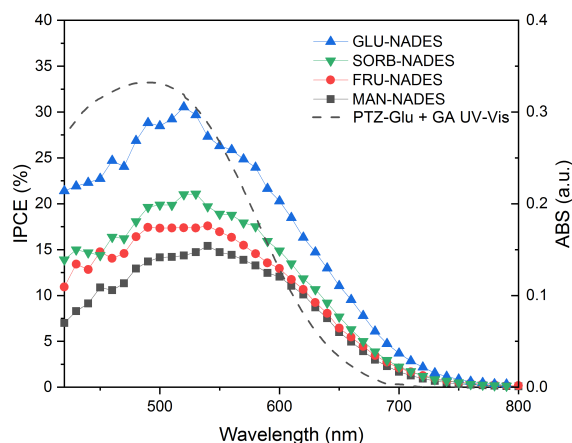
All of the sugar-based NADESs gave similar results, with a slight preference for the GLU-NADES, likely due to the high similarity (same monosaccharide functionality) with the dye and the co-adsorbent. The only NADES displaying a lower performance is MAN-DES. In this case, it seems as though the interaction among **PTZ-Glu**, **GA**, and mannose is not optimal compared to the other combinations (such as **PTZ-Th/CDCA** and **PTZ-Glu/CDCA**).

Figure 2 and Figures S4-6 show a complete and comparative summary of PCE and main PV characteristics. In particular, the photocurrent, which is the most important parameter related to the charge transfer phenomena, has been significantly affected (Figure S4), in contrast with the photovoltage and FF which were similar in all of the systems investigated. The effect on the photocurrent is thus eventually transferred to the PCE of the device. It is evident that the highest efficiencies have been reached for the cells containing **PTZ-Glu** and **GA** in the sugar-based NADES (red histogram), while the performance in the other tested conditions is highly variable but generally lower.



**Figure 2.** Histograms comparing the efficiency as a function of dye, co-adsorbent and sugar-based NADES.

Incident Photon-to-Current Efficiency (IPCE) curves have been measured for the best performing cells (**PTZ-Glu/GA**) in various NADESs. Figure 3 shows the IPCE plots in comparison with the absorption spectra of the sensitized TiO<sub>2</sub> films.<sup>[11a]</sup> In all of the cases, IPCE curves resemble the UV-Vis spectrum of **PTZ-Glu** with 1:10 **GA** on TiO<sub>2</sub> film (Figure 3, dashed line), with a red shift in the peak and band, which might be due to the specific interaction with the NADES medium. The shape of the curves is similar in different NADESs with a wide absorption throughout the entire visible range and a maximum at ca. 530 nm. The trend of IPCE curves is consistent with similar performance of the cells regardless of the NADES nature. In particular, the highest IPCE values have been recorded for the cell using the GLU-NADES, with a satisfactory maximum of ca. 30%.



**Figure 3.** IPCE curves of best-performing DSSC.

Electrochemical Impedance Spectroscopy (EIS) measurements were carried out on the same most performing cells sensitized by **PTZ-Glu/GA** in order to deeper investigate interfaces and charge recombination phenomena.<sup>[17]</sup> An EIS experiment consists in a small sinusoidal voltage stimulus of a fixed frequency applied to the device, with the current response simultaneously measured. By sweeping the frequency over several orders of magnitude (generally from a few mHz to several MHz) it is possible to study the behaviour of the electrochemical system. The analysis of the impedance spectra was performed in terms of Nyquist plots where the imaginary part of the impedance is plotted as a function of the real part of the range of frequencies. Under dark conditions, at open circuit voltage potential, the properties of the sensitized TiO<sub>2</sub>/electrolyte interface can be derived from the Nyquist plot in terms of recombination resistance ( $R_{rec}$ ) and chemical capacitance ( $C_{\mu}$ ), which have been obtained by fitting the data with a proper equivalent circuit.<sup>[8a]</sup> The apparent electron lifetime  $\tau_n$  can thus be calculated from  $\tau_n = R_{rec} \times C_{\mu}$ .<sup>[17a, 18]</sup>

The parameters resulting from fitting the data are listed in Table 5. Even if recombination resistance and chemical capacitance vary among the different cells, the calculated electron lifetimes well match the  $V_{oc}$  trend, with longer lifetime for MAN-NADES in correspondence with the highest measured  $V_{oc}$  (546 mV), followed by that of GLU-NADES cells (527 mV) (see Table 3).

**Table 5.** Cell parameters obtained from Nyquist plots after fitting data.

NADES	$C_{\mu}$ ( $10^{-4}$ F cm <sup>-2</sup> )	$R_{rec}$ (k $\Omega$ cm <sup>2</sup> )	$\tau_n$ (ms)
GLU-NADES	1.2	6.7	0.80
SORB-NADES	0.34	11.4	0.39
FRU-NADES	1.5	5.2	0.77
MAN-NADES	0.61	14.7	0.90

## Conclusion

In conclusion, four sugar-based NADESs have been tested as eco-friendly solvents in DSSCs in the presence of two phenothiazine-based sensitizers. The different nature of the end-substituent of the nitrogen atom in the phenothiazine donor core (glucose functionality vs alkyl chain) was critical to gain control of



constructive directional interactions amongst the different molecular components of the device (photosensitizer, co-adsorbent, and NADES medium). Different set of experiments have been carried out to distinctively investigate the role of the different dye, co-adsorbent, and NADES.

Although it is awkward to have a direct evidence of the presence of intermolecular directional interactions, the overall data point towards a cooperative interplay between the three key components, resulting in an enhanced device PCE. In particular, the best combination originates from the three components carrying or being constituted by a glucose derivative. In our previous work, which was focused on hydrogen generation and that included DSSC data starting from the same glucose-based dye and co-adsorbent,<sup>[11a]</sup> the combination of **PTZ-Glu/GA** in DSSC in a conventional organic medium as the electrolyte solvent did not afford any significant improvement in the performances of the device. Accordingly, also in this work, the presence of these two components was not enough to produce a significant efficiency enhancement. This supports the conclusion that the simultaneous presence of three sugar-based components in the NADES medium is most probably responsible for the best enhancements observed.

This work emphasises the importance of controlling the phenomena taking place at the interface through specific intermolecular interactions involving different key components of the device and the electrolyte solvent, which, in the specific case, not only displays an active role in the performance enhancement, but also represents a natural, bio-renewable reaction medium particularly suitable for a completely eco-friendly industrial scale-up.

## Experimental Section

### Materials and methods

All common reagents were obtained from a commercial supplier (Sigma-Aldrich) at the highest purity grade and used without further purification. The photosensitizers PTZ-Glu and 3,3'-(5,5'-(10-octyl-10H-phenothiazine-3,7-diyl)bis(thiophene-5,2-diyl))bis(2-cyanoacrylic acid) (PTZ-Th) have been prepared according to the literature.<sup>[11b, 14]</sup> The co-adsorbents chenodeoxycholic acid (CDCA) (Sigma-Aldrich), glucuronic acid (GA) (Sigma-Aldrich), D-glucose (Sigma-Aldrich), D-sorbitol (Sigma-Aldrich), D-fructose (Sigma-Aldrich), D-mannose (Sigma-Aldrich), choline chloride (ChCl) (Alfa Aesar) and glycerol (Gly) (Alfa Aesar) have been obtained from a commercial supplier and used without further purification. FTO-coated glass plates (2.3 mm thick; sheet resistance ~7 ohm per square; Sigma-Aldrich) and Dyesol 18NR-T TiO<sub>2</sub> blend of active 20 nm anatase particles were purchased from commercial suppliers. UV-O<sub>3</sub> treatment was performed using Novascan PSD Pro Series-Digital UV Ozone System. The thickness of the layers was measured by means of a VEECO Dektak 8 Stylus Profiler.

**NADESs preparation.** Natural Deep Eutectic Solvents (NADESs) [GLU-NADES: D-glucose/ChCl (1:2 mol mol<sup>-1</sup>); SORB-NADES: D-sorbitol/ChCl (1:1 mol mol<sup>-1</sup>); FRU-NADES: D-fructose/ChCl (2:1 mol mol<sup>-1</sup>); MAN-NADES: D-mannose/choline chloride (2:5 mol mol<sup>-1</sup>)] were prepared by heating under stirring at 60–90 °C for 40–50 min the corresponding individual components until a clear solution was obtained.

**NADES-DSSC preparation.** DSSCs have been prepared adapting a procedure reported in the literature.<sup>[19]</sup> In order to exclude metal contamination, all of the containers were in glass or Teflon and were treated with EtOH and 10% HCl prior to use. Plastic spatulas and tweezers

have been used throughout the procedure. FTO glass plates were cleaned in a detergent solution for 15 min using an ultrasonic bath, rinsed with pure water and EtOH. After treatment in a UV-O<sub>3</sub> system for 18 min, the FTO plates were treated with a freshly prepared 40 mM aqueous solution of TiCl<sub>4</sub> for 30 min at 70 °C and then rinsed with water and EtOH.

A transparent layer of 0.20 cm<sup>2</sup> was screen-printed using a 20-nm transparent TiO<sub>2</sub> paste (Dyesol 18NR-T). The coated transparent film was dried at 125 °C for 5 min. The coated films were thermally treated at 125 °C for 5 min, 325 °C for 10 min, 450 °C for 15 min, and 500 °C for 15 min. The heating ramp rate was 5–10 °C/min. The sintered layer was treated again with 40 mM aqueous TiCl<sub>4</sub> (70 °C for 30 min), rinsed with EtOH and heated at 500 °C for 30 min. After cooling down to 80 °C, the TiO<sub>2</sub> coated plate was immersed into a 0.2 mM solution of the dye in the presence of the co-adsorbent (typically 1:10 glucuronic acid) for 20 h at room temperature in the dark.

Platinum-based counter electrodes were prepared according to the following procedure: a 1-mm hole was made in a FTO plate, using diamond drill bits. The electrodes were then cleaned with a detergent solution for 15 min using an ultrasonic bath, 10% HCl, and finally acetone for 15 min using an ultrasonic bath. Then, a 10 μL of a 5 × 10<sup>-3</sup> M solution of H<sub>2</sub>PtCl<sub>6</sub> in EtOH was added and the electrodes were thermally treated at 500 °C for 30 min.

The dye adsorbed TiO<sub>2</sub> electrode and the counter electrode were assembled into a sealed sandwich-type cell by heating with a hot-melt ionomer-class resin (Surlyn 30-μm thickness) as a spacer between the electrodes.

The electrolyte solution was prepared by mixing at room temperature iodine (20 mM) and PMII (2 M) in different NADESs, and kept in the dark in the air. The electrolyte solution was used within one week from preparation. A drop of the electrolyte solution was added to the hole and introduced inside the cell by vacuum backfilling. Finally, the hole was sealed with a sheet of Surlyn and a cover glass. A reflective foil at the back side of the counter electrode was taped to reflect unabsorbed light back to the photoanode.

**NADES-DSSC measurements.** Photovoltaic measurements of DSSCs were carried out using a 500 W xenon light source (ABET Technologies Sun 2000 Solar Simulator). The power of the simulated light was calibrated to AM 1.5 (100 mW cm<sup>-2</sup>) using a reference Si photodiode. Values were recorded immediately after cells assembling. I–V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. Incident photon-to-current conversion efficiencies (IPCEs) were recorded as a function of excitation wavelength (between 300–800 nm), using a monochromator (HORIBA Jobin Yvon) and a 400 W xenon lamp as incident light, in AC mode. The monochromatic light was mechanically chopped (chopping frequency of 1 Hz) and the AC-photocurrent response was measured using a lockin-amplifier. A white light bias (0.3 sun) was applied to the sample during IPCE measurements.

**Electrochemical impedance spectroscopy.** Electrochemical Impedance Spectroscopy (EIS) spectra were obtained using a Bio-Logic SP-240 galvanostat-potentiostat with EIS option. Measurements were performed in the 100 kHz - 0.1 Hz frequency range under dark conditions at the open circuit potential. The resulting impedance spectra were fitted with the EIS Spectrum Analyser software.<sup>20</sup>

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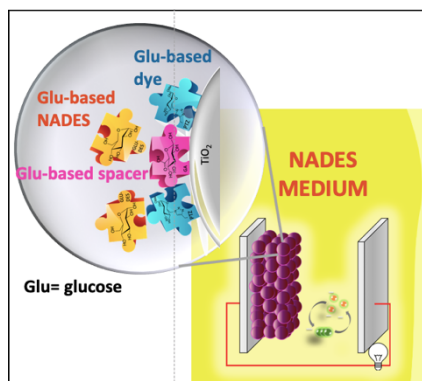
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**Keywords:** deep eutectic solvents • solar energy • photovoltaics • glucose • hydrogen bond

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Sugar-based Natural Deep Eutectic Solvents (NADESs) were used for the first time as active smart environmentally responsible electrolyte solvents in the solar energy production by exploiting the cooperative interactions between the solar device molecular components and NADESs themselves.