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Designing Eco-Sustainable Dye-Sensitized Solar Cells by the Use of a Menthol-based Hydrophobic Deep Eutectic Solvent as an Effective Electrolyte Medium

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Abstract:	This work reports, for the first time, the use of a hydrophobic deep eutectic solvent (DES) as truly eco-friendly electrolyte medium. The hydrophobic DES, consisting in a DL-menthol-acetic acid (1:1 molar ratio) mixture, has been tested in dye-sensitized solar cells in the presence of a de-aggregating agent and a representative hydrophobic organic photosensitizer. The corresponding DES-based devices displayed relatively good power conversion efficiencies in very thin active layers. In particular, the higher cell photovoltage detected in comparison to devices based on toxic and volatile organic compounds may stem from a more efficient interface interaction, as suggested by EIS studies showing greater charge recombination resistance and electron lifetime.

Author Comments:

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Dr. Haymo Ross
Editor
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Dear Dr. Ross,

We are submitting a manuscript entitled:

"Designing Eco-Sustainable Dye-Sensitized Solar Cells by the Use of a Menthol-based Hydrophobic Deep Eutectic Solvent as an Effective Electrolyte Medium"
by Chiara L. Boldrini, Norberto Manfredi, Filippo M. Perna, Vito Capriati,* and Alessandro Abbotto*

for the consideration of publication in Chemistry - A European Journal as a Communication.

Increasing environmental awareness has pressured companies to become more proactive in addressing public concerns related to the environmental effects of products during use and as waste, and to drive the field of technology toward more green practices. The use of renewable feedstocks, which is one of the 12 principles of Green Chemistry, is seen by many as an important strategy towards sustainable development. In this perspective, Deep Eutectic Solvents (DESs), easily obtainable by mixing and gently warming two or three naturally occurring substances, represent a novel and promising class of unconventional, bio-based solvents, potential substitutes of the classical petroleum-derived volatile organic compounds (VOCs), with yet unexplored applications in particular in the field of solar technology.

The need for VOC-free electrolytes in dye sensitized solar cells (DSSCs) has recently gathered much interest, as confirmed by many recent reports, a selection of which is: Bella, F.; Gerbaldi, C.; Barolo, C.; Gratzel, M., Aqueous dye-sensitized solar cells. Chem. Soc. Rev. 2015, 44 (11), 3431-3473; Wu, J.; Lan, Z.; Lin, J.; Huang, M.; Huang, Y.; Fan, L.; Luo, G., Electrolytes in Dye-Sensitized Solar Cells. Chem. Rev. 2015, 115 (5), 2136-2173; Wang, M.; Grätzel, C.; Zakeeruddin, S. M.; Grätzel, M., Recent developments in redox electrolytes for dye-sensitized solar cells. Energy Environ. Sci. 2012, 5, 9394-9405.

On the other hand, the use of water-based electrolytes is typically associated to low power conversion efficiencies and short stability due to desorption of the sensitizer from the semiconductor surface in the aqueous medium. Literature on alternatives liquid electrolytes for DSSCs is pretty rare and to date studies on the effectiveness of hydrophobic DESs as electrolytes for DSSCs are unknown.

Building on our previous findings on water-based DES electrolytes for DSSCs (Boldrini, C. L.; Manfredi, N.; Perna, F. M.; Trifiletti, V.; Capriati, V.; Abbotto, A., Dye-Sensitized Solar Cells that use an Aqueous Choline Chloride-Based Deep Eutectic Solvent as Effective Electrolyte Solution. Energy Technology 2017, 5, 345-353), this work describes an unprecedented use of a hydrophobic menthol-based DES as a supporting electrolyte in DSSCs, as an alternative to a common volatile organic compound (VOC), which is typically used. The corresponding cells have been characterized using photovoltaic and electrochemical techniques. The new DES-based devices showed good power conversion efficiencies, and displayed higher photovoltages compared to the traditional VOC-based cells because of a more efficient interface interaction with the medium. These results open the floodgates to the development of novel eco-compatible and sustainable liquid DSSCs, thereby facilitating the transition towards an industrial development.

Recently, this Journal has devoted much attention to the development of solar technologies, especially solar cells (see for instance: Chen et al., Synthesis of 3H-Benzo[e]indoline and Its Application to Small-Molecule Organic Solar Cells. Chem. Eur. J. 2018, 24, 8747-8750; Li et al., High Performance of 3D Symmetric Flowerlike Sb2S3 Nanostructures in Dye-Sensitized Solar Cells. Chem. Eur. J. 2018, 24, 1-8; Nar et al., Ferrocenyl Phthalocyanine as Donor in Non-Poly(3-hexylthiophen-2,5-diyl) Bulk

Heterojunction Solar Cell. Chem. Eur. J. 2018, 24, 6946-6949; Zhang et al., Ullazine Donor-π bridge-Acceptor Organic Dyes for Dye-Sensitized Solar Cells. Chem. Eur. J. 2018, 24, 5939-5949; Wang et al., A Reusable N-Doped-Carbon-Coated Mo2C Composite Counter Electrode for High-Efficiency Dye-Sensitized Solar Cells. Chem. Eur. J. 2017, 23, 17311-17317), and to the use of DES (García-Álvarez et al., The Future of Polar Organometallic Chemistry Written in Bio-Based Solvents and Water. Chem. Eur. J. 2018, 10.1002/chem.201802873; Marset et al., Deep Eutectic Solvents as Reaction Media for the Palladium-Catalysed C−S Bond Formation: Scope and Mechanistic Studies. Chem. Eur. J. 2017, 23, 10522-10526; Iwanow et al., Preparation of Supported Palladium Catalysts using Deep Eutectic Solvents. Chem. Eur. J. 2017, 23, 12467-12470; Söldner et al., Preparation of Magnesium, Cobalt and Nickel Ferrite Nanoparticles from Metal Oxides using Deep Eutectic Solvents. Chem. Eur. J. 2016, 22, 13108-13113). Thus, we expect this manuscript (a) will provide important and timely information to the chemistry community interested in how to realize novel device architectures for solar cells at the interface between sustainable chemistry and engineering of solar energy conversion and (b) will offer new insights into DES compatibility, which is essential for developing new and more efficient DES-based solar technologies.

We believe that this work meets the requirement for quality, originality and significance as it reports new advances for the development of alternative sustainable technologies with significant practical impact and of broad interest, and that Chemistry - A European Journal, because of its large and diversified audience, appears as an ideal vehicle for the dissemination of this research. We confirm that all co-authors have read and approved the submission of the manuscript, which has not been published previously and is not under consideration by any other Journal. We look forward to hearing the comments of the referees.

Thank you very much for your consideration.

Sincerely,

Vito Capriati and Alessandro Abbotto

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Designing Eco-Sustainable Dye-Sensitized Solar Cells by the Use of a Menthol-based Hydrophobic Deep Eutectic Solvent as an Effective Electrolyte Medium

Chiara Liliana Boldrini,[a] Norberto Manfredi,[a] Filippo Maria Perna,[b] Vito Capriati,*[b] and Alessandro Abbotto*[a]

Abstract: This work reports, for the first time, the use of a hydrophobic deep eutectic solvent (DES) as truly eco-friendly electrolyte medium. The hydrophobic DES, consisting in a DL-menthol-acetic acid (1:1 molar ratio) mixture, has been tested in dye-sensitized solar cells in the presence of a de-aggregating agent and a representative hydrophobic organic photosensitizer. The corresponding DES-based devices displayed relatively good power conversion efficiencies in very thin active layers. In particular, the higher cell photovoltage detected in comparison to devices based on toxic and volatile organic compounds may stem from a more efficient interface interaction, as suggested by EIS studies showing greater charge recombination resistance and electron lifetime.

The increase in energy demand requires alternative and renewable energy technologies,[1] in particular, new photovoltaic (PV) tools aiming to easy-to-fabricate, efficient, and low-cost devices.[2] In the last two decades, much attention has been paid to hybrid organic-inorganic thin film systems, such as dye-sensitized solar cells (DSSCs)[3] and perovskite solar cells.[4] DSSCs are based on a photo-active anode, comprising an inorganic n-type semiconductor layer (typically TiO_2) sensitized by a molecular organic or organometallic dye, a counter-electrode, and a liquid electrolyte that completes the circuit and allows dye regeneration. Hanaya et al. reported a 14.7% record efficiency using liquid electrolyte.[5] Therefore, liquid DSSCs may be playing an important role in the future industrial development of low-cost solar cells with high power energy conversion efficiencies (PCEs).

One of the main drawbacks of liquid DSSCs is the presence of a toxic and volatile organic compound (VOC) as electrolyte, typically acetonitrile or a mixture of aliphatic nitriles. Indeed, leakage or evaporation of the VOC solvent produces a negative environmental impact and seriously limits the temporal stability of the PV efficiency. Thus, the presence of these VOCs is the most critical aspect from the standpoint of “greenness” as it hampers a truly sustainable development of the DSSC technology and prevents its widespread industrial use. The replacement of the organic liquid medium with water-based electrolyte,[6] solid or quasi-solid[3a, 7] electrolyte or hole transporting material in a solid DSSC[8] circumvents this issue, but at the expenses of much lower PCEs.

Deep eutectic solvents (DESs) are an emerging class of unconventional solvents (cheap, thermally stable, non-flammable, non-toxic, and biodegradable) usually made by two or three safe and inexpensive components able to engage in reciprocal hydrogen-bond interactions to form a eutectic mixture with a melting point far below those of the individual components, due to self-association.[9] Because of their minimal ecological footprint, DESs are progressively replacing VOCs in several fundamental and applied processes.[10] They have been primarily investigated in extraction and separation processes,[11] for metal electrodeposition,[10a] in material sciences,[12] but have recently gained increasing attention also in other hot fields of science such as metal-,[13] bio-,[14] and organocatalysis,[15] photosynthesis and electrochemistry,[16] and organometallics[13c,17] with surprising and unexpected results.

The vast majority of DESs described in the literature are hydrophilic, and thus unstable in water. Conversely, hydrophobic DESs have been developed only very recently. In 2015, Kroon et al. first reported the preparation and the usefulness of hydrophobic DESs, consisting of a fatty acid and a quaternary ammonium salt, for the recovery of volatile fatty acids from diluted aqueous solution,[18] and for CO_2 capture.[19] Hydrophobic DESs consisting of decanoic acid and lidocaine in various proportions proved to be effective as well for the removal of metal ions from non-buffered water.[20] In parallel, Marrucho et al. synthesized and characterized novel hydrophobic mixtures composed of DL-menthol and naturally occurring carboxylic acids, and tested (a) their extraction efficiencies towards biomolecules,[21] and (b) for the extraction of pesticides from aqueous environment.[22] A tailor-made hydrophobic DES from methyl trioctyl ammonium chloride and 1-butanol has also been recently set up by Su and co-workers, and showed the highest extraction yield of bioactive Artemisinin from *Artemisia annua* leaves.[23]

Our efforts of late have focused on the development of more environmentally friendly DSSCs, by combining highly hydrophilic choline chloride-based DESs with a specifically designed hydrophilic photosensitizer, which showed PCEs up to 1.9% at 0.5 sun, thereby comparable with the use of a conventional organic VOC medium or water under the same conditions.[24] Building on these studies, in this report we disclose the first use in the field of solar energy of a menthol-based hydrophobic DES as an alternative and promising eco-friendly

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and low-cost medium for liquid DSSCs exhibiting PV efficiency which well compares with VOC-based DSSCs. It is worth underlying that the employment of an hydrophobic, in place of the more common hydrophilic, DES allows the use of conventional, hydrophobic dyes as DSSC sensitizers, including the most efficient systems reported in the literature.[5] This obviates the need to both adapt the molecular structure and to design new dyes for the aqueous media.

We have selected as a representative sensitizer a phenotiazine-based hydrophobic dye containing a terminal 8-carbon atom alkyl chain (**PTZ-ALK**, Figure 1, inset) that we have previously employed both in DSSCs[25] and in the photocatalytic production of hydrogen.[26] The DL-menthol-acetic acid (1:1 molar ratio) eutectic mixture has been selected as a representative hydrophobic DES because it displays very low viscosity compared to the other menthol-based eutectic mixtures developed.[21]

DSSC cells have been prepared using **PTZ-ALK** as a sensitizer in the presence of chenodeoxycholic acid (CDCA) as a disaggregating co-adsorbent[27] in a 1:1 dye:CDCA ratio, as optimized in our previous work on DSSCs using the same dye.[26] A 2.5-µm-thick transparent TiO_2 layer has been selected as the active layer since it gave the best results in our previous work on DES-based DSSCs.[24] Other thicknesses and opaque active layers and dye:CDCA ratios were tested but the results were worse than those of the selected conditions (Tables S1, S2). The electrolyte medium is a DL-menthol-acetic acid (1:1) eutectic mixture, which has been further diluted with 10% v/v EtOH to improve solubility of the electrolyte components. The properties of DES-based DSSCs have been compared with DSSCs featuring the same components (semiconducting layer, sensitizers, electrolyte composition), but containing the conventional acetonitrile/valeronitrile 85:15 mixture as an electrolyte solvent.

The results are summarized in Table 1 and in Figure 1. The PCE of the DES-based cell was 2.5%. These data well compare with our previous report on hydrophilic DES in DSSCs,[24] thus confirming the suitability of hydrophobic DES in DSSCs.[21-23] The unconventional hydrophobic DES brings a number of advantages, such as the use of routine alkyl-substituted record DSSC sensitizers, but without depressing the overall efficiency of the cell. The efficiency of the reference VOC cells was ~ 4%, in agreement with literature values for similar di-branched sensitizers.[25-26,28] PCE of DES- and VOC-based cells are almost in the same range of values, which is encouraging for future studies where more performing dyes and photoanodes, such as those yielding record efficiencies, might be used.

A more detailed look at the PV characteristics revealed that the lower conversion efficiency mainly arises from the lower photocurrent, which is almost twice larger in the case of the VOC-based electrolyte. This result is expected since the presence of a viscous medium such as the hydrophobic DES weakens charge and mass transport in the electrolyte, thus leading to reduced currents. In contrast, fill factors were similar in both types of cells. What is more important, photovoltage of the DES-based device resulted higher than that of the corresponding VOC-based DSSC. The latter result is noteworthy in view of optimal PV characteristics in connecting cells to modules and panels.

Table 1. DSSC parameters with DES- and VOC-based electrolyte.[a]

Cell	Electrolyte	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	R_{rec} (Ω cm^2)	C_μ (F cm^{-2})	τ_n (ms)
1	VOC	533	11.2	66	4.0	0.4	1.1×10^{-4}	0.05
2	DES	585	6.6	65	2.5	1.0	6.1×10^{-5}	0.06

[a] 2.5-µm-thick transparent TiO_2 layer, 1:1 dye:CDCA ratio, Z960 electrolyte solution with DES or VOC as solvent.

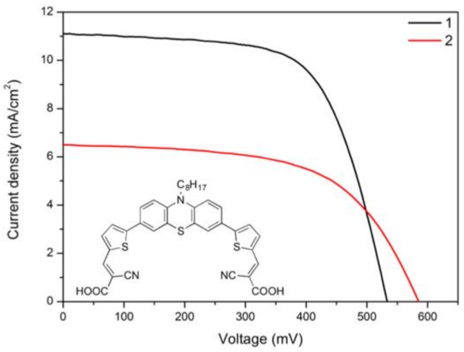

Figure 1. J/V characteristics of DSSC with organic or DES based electrolyte; inset: structure of molecule **PTZ-ALK**

The incident photon to current efficiency (IPCE), that is the external quantum efficiency of the PV cell, has been measured (Figure S1). The IPCE spectra cover the whole visible range, in agreement with the absorption spectrum of the sensitizer adsorbed onto a TiO_2 photoanode,[29] with a peak of nearly 50% from ca. 490 to 560 nm for DES-based cell and of about 70% for the VOC-based one. The efficiencies match the different photocurrents measured. The shape of the IPCE spectrum also closely resembles that of the device containing the hydrophilic DES,[24] however, with an enhancement in the photoconversion likely due to a better charge transport in the electrolyte.

Since we expect that the role of the hydrophobic DES, in comparison with the VOC solvent, should be more critical at the different interfaces involving the electrolyte medium (in particular the dye-TiO_2/electrolyte interface), we decided to use electrochemical impedance spectroscopy (EIS) to focus on interfaces and charge recombination phenomena.[30] In an EIS experiment, a small sinusoidal voltage stimulus of a fixed frequency is applied to an electrochemical cell and its current response measured. The behaviour of an electrochemical system can be investigated by sweeping the frequency over several orders of magnitude (generally from a few mHz to several MHz). The analysis of the impedance spectra was performed in terms of Nyquist plots (Figure 2) where the imaginary part of the impedance is plotted as a function of the real part of the range of frequencies. Under soft illumination (0.25 sun), at open circuit voltage conditions, the properties of the sensitized TiO_2/electrolyte interface can be derived from the Nyquist plot in terms of recombination resistance (R_{rec}) and chemical capacitance (C_{μ}), which have been obtained by fitting the data with the equivalent circuit reported in the inset of the corresponding Figure. The apparent electron lifetime τ_n can also be calculated from $\tau_n = R_{rec} \times C_{\mu}$.[30a, 31] The results of the EIS investigation are summarized in Table 1.

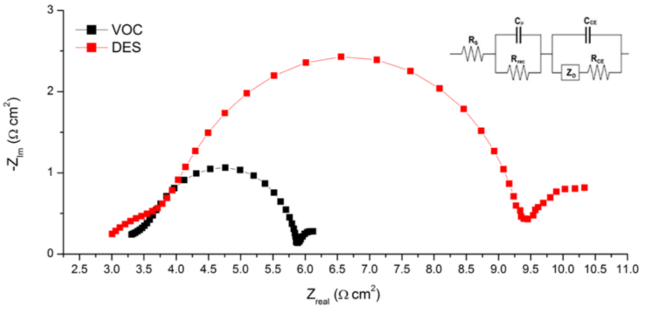

Figure 2. EIS data plots of DSSCs 1 and 2 from Table 1 with VOC- and DES-based electrolyte, respectively.

Remarkably, the relevant EIS parameters collected in Table 1 show that the interface phenomena operating in the VOC- and DES-based devices are substantially different. The most critical parameter is the charge recombination resistance between the sensitized oxide and the electrolyte, which controls the extent of the detrimental charge recombination, that is the back-transfer of electrons from TiO_2 to the oxidized form of the electrolyte redox species. In particular, a smaller R_{rec} indicates a faster charge recombination and therefore a larger dark current and a lower device voltage.[3a] Since the recombination resistance controls how the generated charge may be lost, this parameter is key for the maximum performance attainable for the cell.

Most notably for the scope of this work, the R_{rec} value of the DES-based DSSC is more than twice higher than that of the conventional device based on the VOC medium, thus showing that charge recombination rates are much smaller in the former cell. This finding suggests that the presence of the hydrophobic DES solvent in place of the conventional organic medium positively affects the critical dye-TiO_2/electrolyte interface, thereby minimizing unwanted pathways and possibly improving performances. Accordingly, (a) the cell photovoltage of the DES-based cell is significantly higher (Table 1), improving from 0.53 V in the VOC electrolyte to almost 0.6 V, and (b) the electron lifetime of the DES-based cell resulted higher than that of the VOC-device, though in this case differences are smaller due to the higher chemical capacitance of the latter.

In conclusion, we have investigated an environmentally friendly hydrophobic DES as an effective electrolyte in DSSCs affording a PCE value of 2.5%, which well compares with previous literature values for VOC-free (DES and/or aqueous media) liquid DSSCs. Although the stronger viscosity of the DES medium compared to that of the VOC electrolyte is most probably responsible for a lower cell photocurrent, the photovoltage of the thin film DES-DSSC resulted significantly higher. Of note, the EIS investigation unveils that this is the result of the much higher (more than twice compared to VOC) recombination resistance at the dye-TiO_2/electrolyte interface, a key factor for the maximum performance attainable for the cell. This testifies the critical role played by the hydrophobic DES in optimizing interface phenomena. The good performances, the higher voltage and the lower recombination resistances all suggest that the unconventional hydrophobic DES mixtures can play an important role in improving the eco-compatible and sustainable character of liquid DSSCs, thereby facilitating the transition towards an industrial development plan.

Acknowledgements

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Keywords: Sustainable chemistry • Hydrophobic deep eutectic solvent (DES) • Menthol • Dye-sensitized solar cell • Solar energy

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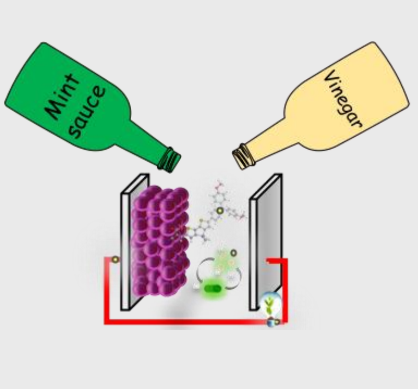
Entry for the Table of Contents

COMMUNICATION

Moving towards sustainable energy solutions! The first environmentally friendly hydrophobic deep eutectic solvent-based dye-sensitized solar cells (DSSCs) have been designed and fabricated. These low-cost solar cells exhibit power energy conversion efficiencies which well compare with those of traditional DSSSc based on toxic and volatile organic compounds.



Chiara Liliana Boldrini, Norberto Manfredi, Filippo Maria Perna, Vito Capriati, and Alessandro Abbotto**

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Designing Eco-Sustainable Dye-Sensitized Solar Cells by the Use of a Menthol-based Hydrophobic Deep Eutectic Solvent as an Effective Electrolyte Medium