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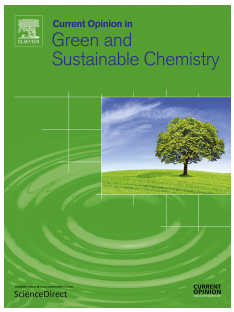

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PII: S2452-2236(18)30116-0

DOI: https://doi.org/10.1016/j.cogsc.2018.11.012

Reference: COGSC 232

To appear in: *Current Opinion in Green and Sustainable Chemistry*

Received Date: 19 November 2018

Revised Date: 22 November 2018

Accepted Date: 27 November 2018

Please cite this article as: M.H. Nematollahi, P.J. Carvalho, Green Solvents for CO_2 Capture, *Current Opinion in Green and Sustainable Chemistry*, https://doi.org/10.1016/j.cogsc.2018.11.012.

Green Solvents for CO_2 Capture

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Abstract

The development of specific “green” solvents with unique combination of properties and associated techniques for target applications, capable of minimizing the environmental impact from their use in chemical production or by developing sustainable and renewable energy and resources, has been gathering increasing attention over the last years. Emerging alternatives or undervalued self-claimed greener solvents, like ionic liquids, amino acid-functionalized ionic liquids, ionic liquid mixed solvents and eutectic solvents, have been proposed as promising materials with unique properties not achievable by means of any other material. Nonetheless, in spite of all these greener compounds outstanding properties and potential for acid gas separation, important limitations have hampered the development of separation units and processes capable of fulfilling industry demands. This study intends to carry a critical analysis upon the solvents proposed for CO_2 capture and the pursued technologies to make Carbon Capture, Utilization and Storage a reality.

Introduction

Concerns with increasing average global temperature due to CO_2 concentration in the atmosphere, with 36.8 gigatons released in 2017 alone, have spurred a worldwide debate on CO_2 emissions, ultimately leading to challenging climate frameworks. Even though gas separation has long been used in natural gas industry, due to the increased value of the post-treated gas, post-combustion is still seen as a non-efficient, costly and, ultimately, unfeasible process.[1–3] Nonetheless, post-combustion technology is particularly appealing to tackle the climate frameworks targets since one can retrofit existing power plants, one of the main sources of anthropogenic CO_2 emissions. Several physical and chemical processes, based on absorption, adsorption, membranes

and cryogenic separation, are commercially available and widely used by the natural gas processing industry.[3] However, when envisioning post-combustion, the current technologies, requiring large separation units and high CO_2 partial pressures, stand unfeasible for post-combustion processes. Thus, innovative post-combustion technological development for removing acid gases, envisioned using green solvents, is indispensable aiming at a clean energy production, anthropogenic CO_2 capture, transportation and/or reconstitution into value-added products.

Although the idea of an "ideal green solvent" suitable for all sorts of chemical transformations sounds unrealistic or even pretentious, the development of specific "green" solvents with unique combination of properties and associated techniques for target applications, capable of minimizing the environmental impact from their use in chemical production or by developing sustainable and renewable energy and resources, has been gathering increasing attention over the last couple of years. Emerging alternatives or undervalued self-claimed greener solvents, like task-specific ionic liquids (ILs), amino acid-functionalized ILs, ionic liquid mixed solvents and eutectic solvents, are promising materials with unique properties not achievable by means of any other material.

A number of interesting reviews have been published during the last few years addressing various aspects of CO_2 capture processes.[2,4–6] This study intends to carry a critical analysis upon the solvents proposed for CO_2 sorption and the pursued technologies to make Carbon Capture, Utilization and Storage (CCUS) a reality (Fig. 1).

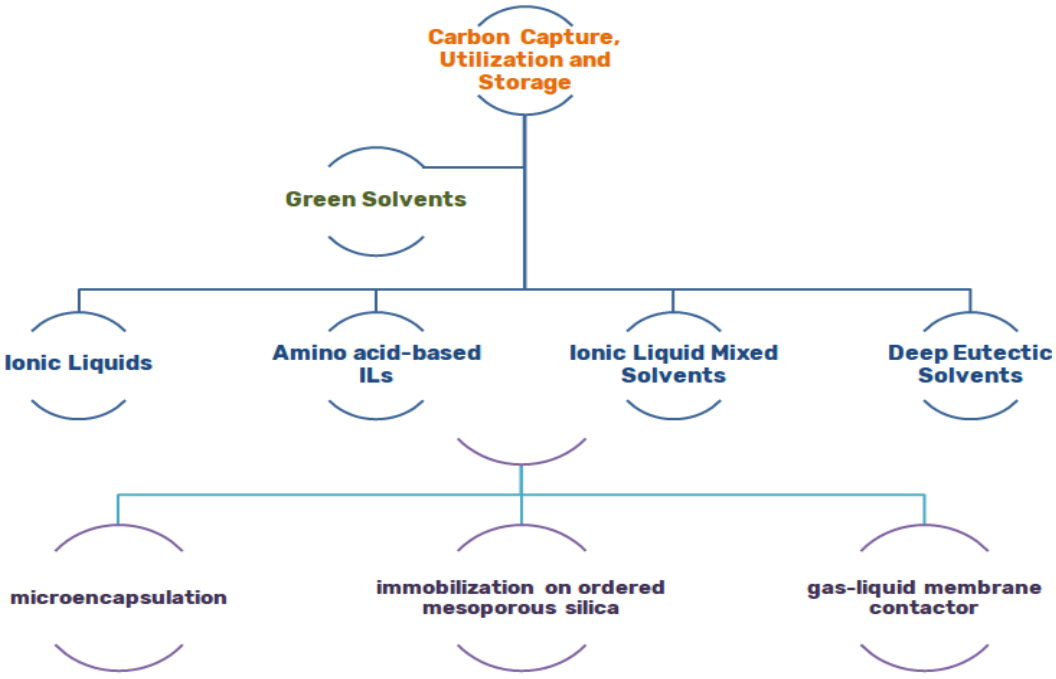

Figure 1. Schematic representation of the Carbon Capture, Utilization and Storage for CO_2 capture.

Ionic Liquids have been, at least for a certain time, considered as not only designer solvents but also as green solvents mainly because their negligible vapor pressure, not contributing thus to the

volatile organic compounds' problematic. But, often their synthesis is not green, many are badly biodegradable and show a significant toxicity.[7] Nonetheless, ILs are so “species-rich”, comprising a large set of chemically very different solvent and liquid classes with remarkably different characteristics - having in common the fact that all are salts and liquid at low to moderate temperatures - that similarly to the term “green solvents” the term ionic liquid becomes almost meaningless. Nonetheless, ILs still retain the label of promising novel solvents for a wide range of potential applications; with their application as solvents for CO_2 capture processes still attracting most of the spotlight. While most ILs, even those highly CO_2-philic, were shown not to be feasible solvents for CO_2 capture,[6,8,9] either because of their similar sorption capacity to common organic solvents or to their high viscosity, leading to the design of unfeasible separation units, many authors have redirected their focus from a simple IL functionalization, like fluorination of either the ionic liquid anion or cation,[10,11] oxygenation of the anion [11] or the use of basic anions or cations, to explore mechanisms of enhancing the CO_2 chemisorption through the optimization of acetate-based ILs or the use of greener precursors like fatty acids, carboxylic acids and amino acids.[12–15]

Amino Acid-based ILs (AA-ILs) are particularly promising because of their low cost, abundant availability, and nontoxic biodegradability.[16] However, although AA-ILs present high chemical absorption capacity [12,17] (Fig. 2) their CO_2 absorption presents important kinetic limitations related to the high viscosity and low diffusion coefficients, that result from the CO_2-complex and the salt bridge hydrogen-bonded network formed upon the reaction with CO_2.[18] Aiming at circumventing these limitations different approaches have been proposed, like the use of a co-solvent able to lower the mixture viscosity and improve mass transfer limitations, the use of a solid phase to immobilize the IL and the use of the IL in membrane gas absorption processes.[13,16,17,19–21] Confining ILs in nanoporous matrices, with one or more of their spatial dimensions subjected to a geometrical restriction, results in nanoconfined ILs with improved mechanical integrity and ionic conductivity that overcomes the major drawbacks of bulk ILs, such as high viscosity, slow gas diffusivity and ultimately, requiring reduced quantities of IL to achieve the same separation.[22] Recently, Palomar’s group [17,23] developed a micro-encapsulation technique to encapsulate ILs in a hollow carbon submicrospheres, with a diameters between 400 and 700 nm, able to retain a large amount of IL (up to 80% in weight) allowing discretizing the IL fluid in micro-drops, increasing drastically the gas−liquid contact surface and ultimately the sorption kinectics.[17,23] The authors reported a dramatic increase in the CO_2 absorption rates, maintaining the high absorption capacity reported for the neat IL.[17] Hiremath et al.[20] proposed a highly reversible CO_2 capture using AA-ILs synthesized from four different amino acid sources immobilized on ordered mesoporous silica. The authors reported fast kinetics (with equilibrium times lower than 30 min), moderate chemisorption and an easy and low energy demanding

desorption processes finely controlled by the suitable amino acid effective loading, temperature and CO_2 concentration.[20]

Membrane gas absorption provides a high specific surface area, independent controllable gas and liquid flow rates, a compact and energy efficient separation unit, and a linear scale-up design. On the other hand, on a gas-liquid membrane contactor the absorbents allow high selectivity and a high mass transfer driving force. Lu et al.[21] proposed the use of a non-dispersive sustainable absorption by a hydrophobic polypropylene micro-porous hollow fiber membrane contactor using the monoethanolamine glycinate amino acid-functionalized IL. The authors reported a high membrane flux and low gas outlet CO_2 concentration, highlighting the potential of the duality "*environmentally friendly and efficient CO_2 absorbent*" and gas-liquid membrane contactor separation unit.[21]

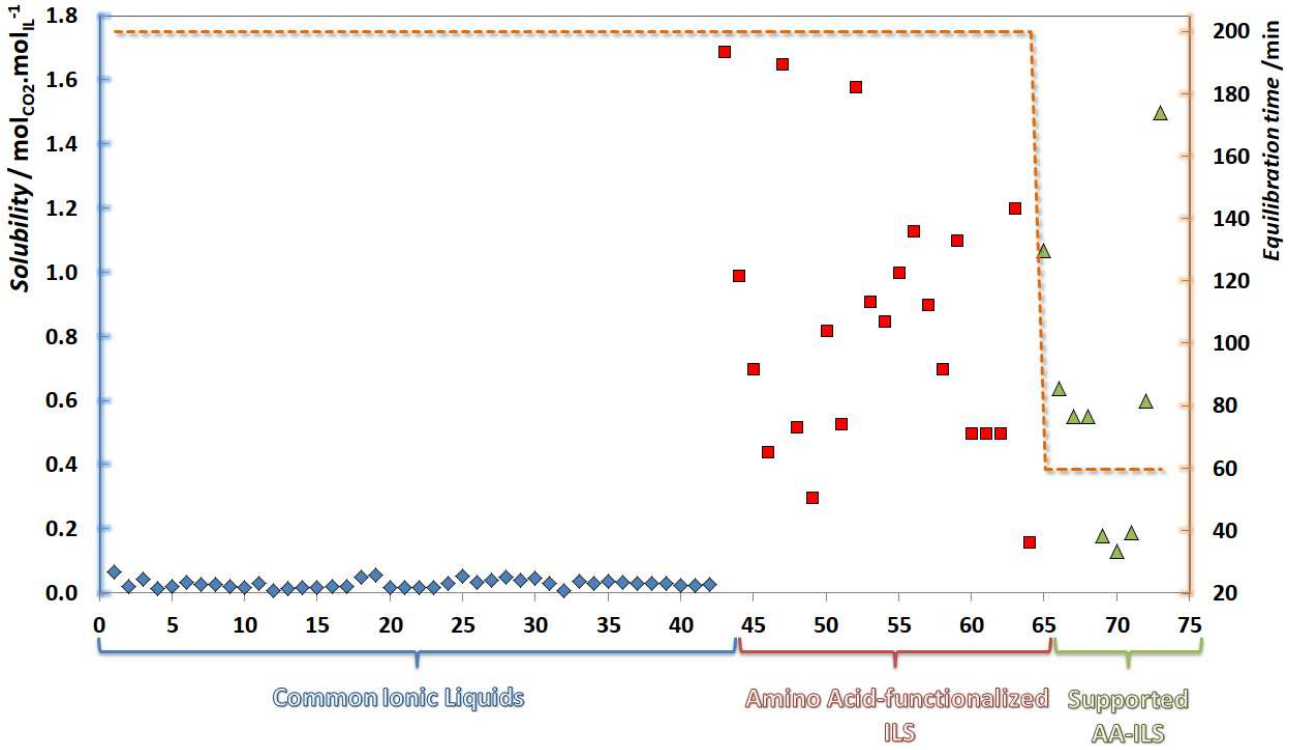

Figure 2. Carbon dioxide solubility and equilibration time of common ILs, amino acid-functionalized ILs and amino acid-functionalized ILs supported in ordered mesoporous silica and hollow carbon submicrospheres.[17,20,24]

Ionic Liquid Mixed Solvents stand as another approach to overcome the known limitations of ILs. Mixtures of ILs with water or organic solvents have been proposed as new absorbents for CO_2 separation.[9] At present, the research on ILs mixed solvents for CO_2 capture focus mainly on IL-water solutions, IL-alkanolamine blends, IL-organic solvents and IL-IL mixtures.[13,14,25–27]

Although not a trivial task, due to the strong dependence on the nature of the constituents ions/compounds, several authors evaluated mixtures of ILs as a mechanism to increase the sorption capacity by manipulating specific interactions, excess volume and viscosity. As reported by Moya et al.[28], mixtures of ILs with unfavorable intermolecular interactions, presenting thus positive

deviations to ideality, show increased CO_2 solubility and favorable transport properties, with negative viscosity deviations, while mixtures with near-ideal behavior present averaged CO_2 absorption capacity of the neat ILs. Although the results denote new opportunities to design IL-based absorbents with better balanced properties for CO_2 capture, its applicability is restricted to physical absorption.[14,28,29] Aiming at overcoming these limitations, IL-amine hybrid solvents have been proposed as energy-saving systems for CO_2 capture, compared to the conventional amine scrubbing process.[14] Ma et al.[30] reported IL-amine hybrid solvents composed of MEA with 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate with 24% to 26% lower energy consumption. However, the amine and CO_2 reaction products impose such a high viscosity to the solvent that hinders pumping or precipitate them from the solvent. Furthermore, the formed carbamate promotes severe corrosion during the absorbent regeneration.[12] Focus on overcoming the problems resulting from the amine and CO_2 reaction, in mixed IL-amine solution, and eliminate the energy requirements, compared with conventional amine scrubbing process, several authors, following the idea proposed by Bara et al.[31,32], evaluated the use of water as a co-solvent.[14,26,27,33,34] As stated by the authors, the IL-amine hybrid solvents have shown to be, through the manipulation of the IL concentration, an energy-saving system for CO_2 capture with reduced heat of absorption and manageable diffusivities and kinetics.[14]

Gómez-Coma et al.[13] aiming at enhancing the CO_2 chemisorption, through the optimization of acetate-based ILs, proposed the use of aqueous solutions of 1-ethyl-3-methylimidazolium acetate in nondispersive absorption in a polyvinylidene fluoride hollow fiber membrane contactor. As reported by the authors a mixture of 70% in volume of IL allows an overall mass transfer coefficient 5 times higher than that obtained for the neat IL, concluding that the use of aqueous solutions allows not only to overcome the known mass transfer limitations but mostly position the solvent as a competitive solvent when compared to traditional alkanolamine solvents.[13]

Deep Eutectic Solvents. The concept of deep eutectic solvents (DES), a mixture of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), has surfaced recently as a new class of solvents with high potential for acid gas separation. Although the definition of the term deep, proposed by Abbott et al.[35], on most of the reported DES is questionable, the advantage of these eutectic solvents on many applications stands indisputable.[36] DES have been proposed for CO_2 capture by Li et al.[37] back in 2008 using an eutectic mixtures composed of choline chloride and urea. Since then, many evaluated other HBD and HBA, like glycerol, ethylene glycol, ammonium-, phosphonium- and amine-based, aiming at enhancing the CO_2 solubility.[38–41] Sze et al.[42] and Bhawna et al.[43] evaluated the DES basicity on the CO_2 sorption by preparing the DES with a

superbase, aiming at promoting the formation of active alkoxide anions through the deprotonation of the HBD and HBA OH groups, reporting increased CO_2 capture. With the increasing number of DES evaluated, the concept of natural DES (NADES) – DES composed of "natural" or of "biological origin" components – has been proposed as a greener class of a DES.[44] However, this term is somewhat misleading, since although most of the components of NADESs occur in living things in many cases they are chemically synthesized for the formulation.

Even though DES have shown high potential for CO_2 capture, the number of experimental studies on gas solubility is remarkable limited to CO_2 and minor studies on SO_2 with studies on carbon capture from complex gas mixtures or selectivity nonexistent. Furthermore, on those available DES are often mixed with a significant amount of water to, similar to the approach followed for the ILs, minimize energy requirements, heat of absorption and mass transfer limitation.[4,45,46] Sarmad and coworkers[45,46] evaluated 35 DES in terms of the influence of salt and HBD type and structure, as well their molar ratio on the CO_2 solubility and viscosity. As reported by the authors, stronger HBA–HBD intermolecular hydrogen bonds lead to lower CO_2 solubility while increasing the alkyl chain length, or the number of carbon atoms, in the HBA or HBD lead to higher CO_2 solubility due to increased free volume within the DES. Among the DES evaluated, the authors highlighted 15 based on glycerol-containing DES and fluorinated ILs, with viscosity lower than 200 mPa·s, as those with the highest CO_2 absorption capacity. Although the CO_2 absorption reported by the authors stand within that reported for conventional ILs, as depicted in Fig. 3, the reduction on the mixture viscosity allowed to achieve better kinetics of absorption. Furthermore, by adding water to the glycerol-based DESs the authors were able to further improve the kinetics of absorption and enhance the mixture CO_2 absorption capacity.[46]

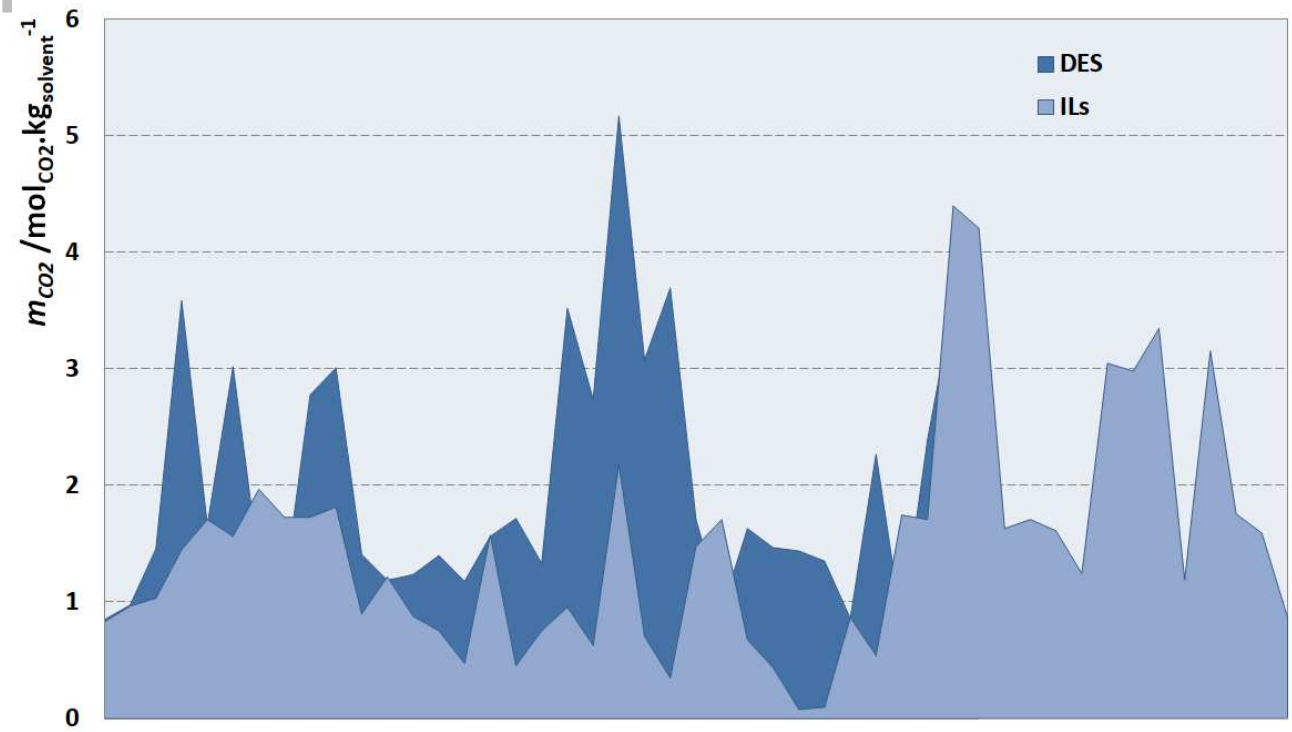

Figure 3. Carbon dioxide molality in DES (dark blue) and in conventional ILs (light blue). Data taken from references [4,45,46].

Summary and future perspectives

Being an energy-intensive process, with almost 80% of the total costs for the whole CO_2 mitigation effort related to the capture process, the development of novel absorbent materials for high-performance post-combustion CO_2 capture stands vital on the pursuit for a sustainable use of fossil fuels in a low-carbon economy with decreasing greenhouse gases emissions. Emerging alternatives or undervalued self-claimed greener solvents, like ionic liquids, amino acid-functionalized ILs, ionic liquid mixed solvents and eutectic solvents, have been proposed as promising materials with unique properties not achievable by means of any other material.

The outstanding thermophysical properties of ILs have gathered a remarkable interest both from industry as academia. The possibility of fine-tune the ILs properties through suitable anion-cation combinations and from the possibility of developing task-specific ILs for target applications allowed to envision ILs as feasible solvents for CO_2 capture. Exploring mechanisms of enhancing the CO_2 chemisorption, the community proposed approaches ranging from the optimization of acetate-based ILs or the use of greener precursors like fatty acids, carboxylic acids and amino acids, to ILs mixed solvents of IL-water solutions, IL-alkanolamine blends, IL-organic solvents and IL-IL mixtures. Deep eutectic solvents, a mixture of a hydrogen bond acceptor and a hydrogen bond donor, has surfaced recently as a new class of solvents with high potential for acid gas separation. Although, DES have shown high potential for CO_2 capture the number of experimental studies on gas solubility is remarkable limited.

Nevertheless, in spite of all these greener compounds outstanding properties and potential for acid gas separation, important limitations have hampered the development of separation units and processes capable of fulfilling industry demands. Academia tends to focus on enhancing equilibrium capacity neglecting other properties, such as transport properties, that impose important penalties on process performance, and therefore on cost, that ultimately prove the process unfeasible. If one aims at developing a technical and economical viable process, for carbon capture, the pursuit on improving CO_2 solubility, viscosity and heat capacity must be addressed from a process engineering perspective. Leclaire and Heldebrant [2], in a recent "*call to arms*" perspective review call the attention to critical research needs, with emphasis on the principles of green chemistry and green engineering, to make carbon capture, utilization and storage a reality.

Aiming at enhancing absorption and desorption processes, several authors have evaluated the use of a solid phase to immobilize the solvents and the use of gas-liquid membrane contactors for gas absorption processes. Although, confining solvents in nanoporous matrices result in improved mechanical integrity capable of overcoming the major drawbacks of the bulk solvents, such as high viscosity and slow gas diffusivity, the technology is still in an initial stage of development with major challenges to be addressed prior to their scale-up and ultimately industrial application. Membrane gas absorption, on the other hand, poses as a mature technology in which high specific surface area, independent controllable gas and liquid flow rates, a compact and energy efficient separation units and a linear scale-up design allows one to envision its use for carbon capture. Aiming at taking advantage of the membrane technology characteristics, several authors proposed the use of gas-liquid membrane contactors for the intended separation. The use of absorbents on a membrane contactor improves the separation selectivity and the mass transfer driving force, allowing high membrane fluxes and low gas outlet CO_2 concentration, highlighting the potential of the technology to take advantage of the green solvents discussed here and make the carbon capture, utilization and storage a reality.

Acknowledgments

This work was developed in the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (ref. FCT UID/CTM/50011/2013) funded by FEDER through COMPETE2020-Programa Operacional Competitividade e Internacionalização (POCI) and by national funds through FCT-Fundação para a Ciência e a Tecnologia. P.J.C. thanks FCT for the contract under the Investigator FCT 2015 (IF/00758/2015).

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