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## Enantiopure natural deep eutectic solvents for metal–organic framework chiral induction†

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**A green alternative approach to the chiral induction of a metal–organic framework (MOF) has been explored using the natural deep eutectic solvents (DES) proline : thymol (1 : 7) and menthol : thymol (1 : 1). These solvents have been successfully employed for the preparation of the MIL-103 MOF and lead to an enantioenrichment of the porous material when used in enantiopure form, as demonstrated by circular dichroism.**

Chiral metal–organic frameworks (CMOFs) represent an interesting class of crystalline porous materials with a broad range of applications in catalysis, optics and separation.<sup>1</sup> The most common approach to the elaboration of CMOFs consists in employing enantiopure building blocks.<sup>2</sup> Albeit successful, this strategy requires the prior preparation of such enantiopure species, either metal nodes or most often organic ligands. This can represent a costly, energy-demanding and time-consuming process, potentially involving multiple steps (protection/deprotection, coupling reaction using metal-based catalysts, for example), the use of chiral reagents and purification using organic solvents. Aiming at reducing the number of steps, the energy consumption and the use of toxic/flammable reagents and solvents, it seems appealing to envision preparing CMOFs from achiral precursors *via* chiral induction based on an enantiopure additive or guest.<sup>3</sup> For this purpose, a variety of chiral additives have been screened and employed in the literature for CMOF chiral induction (Table 1).<sup>4</sup> Hence using representative compounds such as cinchonidine, leucine, proline, carvone, 2-amino-1-butanol, camphoric acid and camphor sulfonate, CMOFs and enantioenriched MOFs

have been reported.<sup>4</sup> However, it is worth noting that, while this process represents a great advancement, it still relies on the solvothermal synthesis of MOFs in toxic and flammable solvents like DMF, DEF or NMP, in the vast majority of these reports (Table 1). An alternative to chiral additive is the development of enantiopure solvents, as such chiral media straightforwardly provide an enantiopure environment (Table 1).<sup>5</sup> In this respect, it has been demonstrated that chiral ionic liquids may be well suited since the large coulombic interactions between the enantiopure components yield a structured organization of the medium reflecting the asymmetry.<sup>5b,c</sup> Despite this successful proof-of-concept, ionic liquids have the drawback of sometimes requiring a purification step in their synthesis and may, themselves, show toxicity.<sup>6</sup> Another class of media, cousin of ionic liquids, that may be considered for this aim is deep eutectic solvents (DESS).<sup>7</sup> DESSs are formed by mixing, in an appropriate molar ratio, two or more species that are usually solids at room temperature and prone to hydrogen bonding. The resulting fluids have a freezing temperature below that of either component, low vapor pressure, relatively wide liquid range, non-flammability and the ability to dissolve polar species.<sup>8</sup> The preparation of these media consisting in the simple mixing of their components, with sometimes an additional heating/cooling step, can be considered green, as it limits the generation of waste and does not require a purification step, in contrast to ionic liquids. Furthermore, DESSs may be composed of naturally occurring compounds,<sup>9</sup> hence of readily accessible enantiopure species affording straightforward access to a variety of green chiral solvents, with potentially lower toxicity and flammability than solvents traditionally employed for solvothermal synthesis. Interestingly, DESSs have demonstrated their adequacy for MOF synthesis,<sup>10</sup> allowing the formation of prototypical materials, impacting their morphology and properties as well as their stability.<sup>11</sup> However, a particular emphasis has been put on the use of DES based on choline chloride and urea derivatives,<sup>12</sup> and, to the best of our knowledge, natural enantiopure DESSs have not been explored as solvents for MOF chiral induction (Fig. 1).

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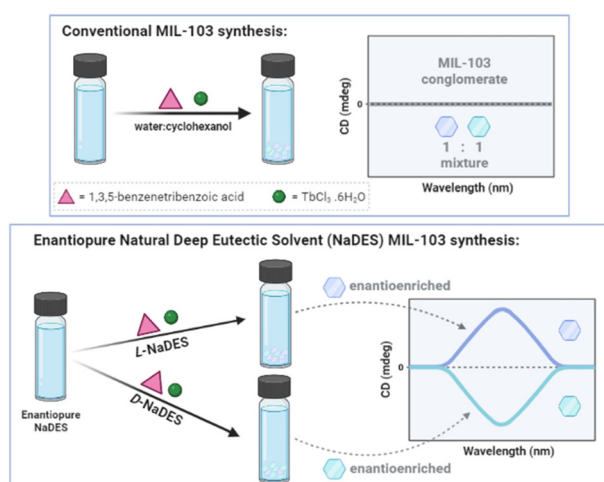
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**Table 1** Comparison of the approach proposed here with selected reported one-pot syntheses of chiral MOFs from achiral precursors

Entry	Solvent	Temperature	Reaction time	Chiral inductor	Ref.
1	DMA	140 °C	2 days	L-Leucine	4a
2	DMF/DEF	120 °C	3 days	(-)-Cinchonidine (+)-Cinchonine	4b
3	Ethylene-urea	140 °C	4 days	(-)-Carvone (+)-Carvone	4c
4	H <sub>2</sub> O : MeOH (1 : 2)	RT	1 week	(-)-Camphoric acid (+)-Camphoric acid	4d
5	NMP : H <sub>2</sub> O (4 : 1)	120 °C	2 days	L-Proline D-Proline	4e
6	DMF : EtOH : H <sub>2</sub> O (5 : 1 : 1)	60 °C	7 days	(R)-(-)-2-Amino-1-butanol (S)-(+)-2-Amino-1-butanol	4f
7	DMSO/MeOH	4 °C	24 h	L-Proline D-Proline L-Menthol D-Menthol	4g
8	1-Butyl-3-methylimidazolium L-aspartate	110 °C	12 days	L-Aspartate	5b
9	1-Ethyl-3-methylimidazolium L-lactate	140 °C	5 days	L-Lactate	5c
10	DMF : H <sub>2</sub> O (1 : 1)	RT	5 days	Low molecular weight gelators	5e
11	(i) D- or L-proline : thymol (1 : 7)  (ii) D- or L-menthol : thymol (1 : 1)	120 °C	3 days	L-Proline D-Proline L-Menthol D-Menthol	This work

**Fig. 1** Strategy for the chiral induction of MOF via the use of enantiopure natural DESs.

Such an approach would represent a green advancement in the field of CMOF preparation, as it constitutes a one-pot strategy without the prerequisite synthesis of chiral building blocks, hence showing a favorable profile in terms of cost, energy and time consumption as well as a limited number of involved chemicals and reagents. In addition, these media may be considered as potential substitutes for flammable solvents commonly employed for solvothermal synthesis, and, depending on the nature of their components, may show limited toxicity, the latter aspect being a matter of current active research.<sup>13</sup>

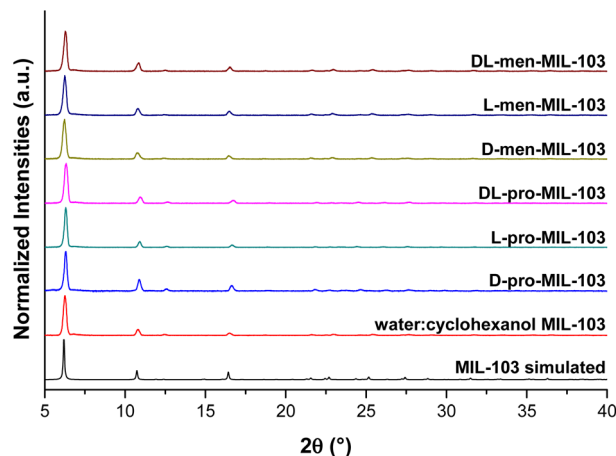
In this work, the use of such chiral DES as green natural media for the preparation and enantioenrichment of a MOF has been investigated. To that aim, the MIL-103 material, Ln

(btb) (Ln = Lanthanide, btb = 1,3,5-benzenetrisbenzoate), was chosen as it crystallizes in the  $R\bar{3}_2$  space group as a conglomerate with each individual crystal comprising either enantiomer resulting from the propeller-like twisted conformation of the btb ligand.<sup>14</sup> Furthermore, a recent report has shown the two-step enantioenrichment of this MOF using first the formation of a complex with lanthanide cations with either L- or D-phenylalanine, followed by a solvothermal reaction with the tricarboxylic acid ligand in a mixture of DMF, methanol and water.<sup>15</sup>

In light of this literature precedent, the use of a carboxylic acid-based chiral DES was envisioned for a one-pot chiral induction process and the proline : thymol (1 : 7) DES was thus selected.<sup>16</sup> Heating a 1 : 1 : 1.8 mixture of  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{btbH}_3$  and NaOH (aq. solution) in D-, L-, or DL-proline : thymol (1 : 7) at 120 °C for 3 days afforded a solid that was washed with water, DMF and EtOH. The material was then further activated by immersion in EtOH for one week with the solution being changed every two days, and then drying at 80 °C in an oven overnight. The solids were characterized by elemental analysis, powder X-ray diffraction, infrared spectroscopy, TGA and  $\text{N}_2$  adsorption-desorption isotherms at 77 K. The powder X-ray diffraction patterns (Fig. 2 and Fig. ESI1†) and the FT-IR spectra (Fig. ESI2†) of the three obtained materials are in agreement with what is expected for this MOF and match those of the reference material prepared under the reported<sup>14</sup> water : cyclohexanol (1 : 1) conditions. Elemental analysis confirmed the expected  $\text{Tb}(\text{btb})(\text{H}_2\text{O})_x$  formula, highlighting the efficiency of the work-up procedure to remove potential impurities such as ligands, salts or components of the DES. Only traces of remaining proline were observed for the D-pro-MIL-103(Tb) and DL-pro-MIL-103(Tb) materials.

TGA analysis under nitrogen demonstrated analogous thermal behavior and stability for the MOFs synthesized from



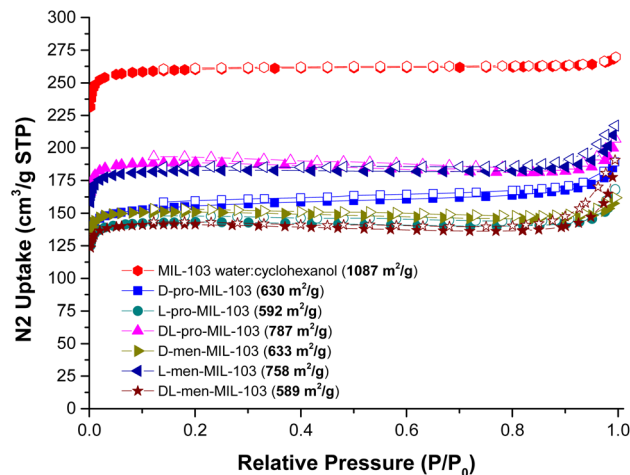


**Fig. 2** PXRD patterns of the MIL-103(Tb) MOFs prepared in different solvents: water : cyclohexanol (1 : 1), D-proline : thymol (1 : 7), L-proline : thymol (1 : 7), DL-proline : thymol (1 : 7), D-menthol : thymol (1 : 1), L-menthol : thymol (1 : 1), and DL-menthol : thymol (1 : 1).

the three DES and water : cyclohexanol (1 : 1) MIL-103(Tb) prepared here as a reference (Table ESI1, Fig. ESI3–6†). A plateau with no major weight loss followed by decomposition at around 578–588 °C was observed for all four materials. The obtained decomposition temperature range was higher than the reported value of *ca.* 400 °C. This difference was expected and can be explained by the fact that TGA analyses were herein performed in the absence of oxygen, unlike the experimental conditions employed for the reported material. Oxygen-free analysis avoids chemical decomposition by oxidation, thus providing higher thermal stability, and consequently, a higher decomposition temperature. Consistently, a plateau until decomposition at around 600 °C has been determined in the literature for the TGA study of MIL-103(La) under N<sub>2</sub>.<sup>17</sup>

The SEM micrographs for the MIL-103(Tb) MOFs prepared from DESs (Fig. ESI28–30†) show a rod morphology that is consistent with what has been reported for MIL-103(La)<sup>17a</sup> and MIL-103(Eu).<sup>17b</sup> Interestingly, block-shaped crystals were observed for the reference MOF prepared from water : cyclohexanol (1 : 1) (Fig. ESI27†). The difference in morphology highlights the impact of the solvents, in particular DES, as previously illustrated for the benchmark materials HKUST-1 and Mg-MOF-74.<sup>11</sup>

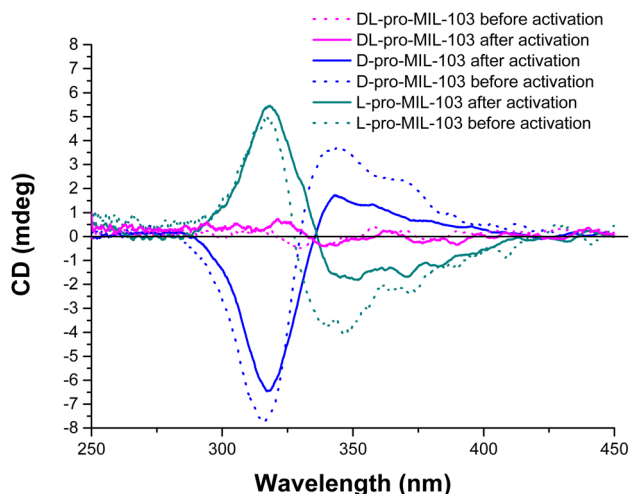
The specific surface area of the MOFs was determined from N<sub>2</sub> adsorption–desorption isotherms at 77 K and calculated by the Brunauer–Emmett–Teller (BET) method (Fig. 3 and Table ESI1†). The microporous DES-synthesized MOFs presented a BET-specific surface area (*S*<sub>BET</sub>) range (592–787 m<sup>2</sup> g<sup>−1</sup>) that was in accordance with the one reported in the literature, albeit slightly lower (730–930 m<sup>2</sup> g<sup>−1</sup>).<sup>14</sup> Notably, the water : cyclohexanol (1 : 1) MIL-103(Tb) MOF, prepared here as a reference, presented a higher *S*<sub>BET</sub> value of 1087 m<sup>2</sup> g<sup>−1</sup>. This may be correlated to the different crystalline morphology. It is worth noting that a similar *S*<sub>BET</sub> value has been reported for MIL-103(La) prepared from DMF/MeOH/H<sub>2</sub>O (3 : 3 : 0.5),<sup>18</sup> once



**Fig. 3** N<sub>2</sub> uptake vs. relative pressure plot of the MIL-103(Tb) MOFs. *S*<sub>BET</sub> values are shown in bold, respectively, for each material, in the legend.

again highlighting the effect of the preparation method on the textural properties. Interestingly, for all materials, a consistent pore distribution was observed with pores of around *ca.* 15 Å (Fig. ESI20–26†). Not only did these results confirm that the porosity of the MOFs prepared in DES is maintained but they also further support the absence of residues or impurities within the pores.

The study by diffuse-reflectance circular dichroism showed signals of opposite magnitudes for the D- and L-MIL-103(Tb) MOFs (Fig. 4). The CD spectra are the same, albeit weaker in intensity, as the ones reported when using a two-step process based on D-/L-phenylalanine.<sup>15a</sup> In their study, Yamada, Narushima and coworkers unambiguously demonstrated the absence of the remaining chiral inductor in the final material and attributed the CD signal around 310 nm to the signature



**Fig. 4** Circular dichroism spectra of MIL-103 MOF(Tb) prepared in different solvents: D-proline : thymol (1 : 7), L-proline : thymol (1 : 7), and DL-proline : thymol (1 : 7), before and after activation.



of the chirality of the propeller-like twisted conformation of the btb ligand, hence of the MOF.<sup>15a</sup> Furthermore, it can be noted that the circular dichroism of free proline is expected at a different spectral range (Fig. ESI7†), strongly supporting the absence of a free residual chiral inductor in the pores of the MOF, in agreement with the above-mentioned results from elemental analysis and TGA. This unequivocally indicates an enantioenrichment of the material itself, dependent on the chirality of the DES component employed for the MOF synthesis. Such an effect was not observed for DL-MIL-103(Tb) prepared in a racemic solvent and for the reference material synthesized in water:cyclohexanol (1:1), as expected for a conglomerate. Interestingly, the activation process involving the immersion of the MOF in EtOH for a week followed by drying at 80 °C had limited impact on the CD signal, showing the stability of the MOF.

In order to assess whether this approach can be extended to other lanthanides, MIL-103(Nd) and MIL-103(Eu) were prepared under the same experimental conditions. The materials were characterized by X-ray powder diffraction (Fig. ESI8–12†), confirming their identity, and then by diffuse-reflectance circular dichroism (Fig. 5). As for MIL-103(Tb), opposite signals were observed depending on the chirality of the proline composing the DES used for synthesis. For the three MOFs, a negative Cotton effect was consistently observed when using L-proline, whereas it was positive in the case of the MOF prepared from the D-proline-based DES. This consistency highlights the impact of the chirality of the DES on the enantioenrichment of the MOF. The difference in the signal intensity depending on the nature of the lanthanide can be related to the different sizes of the  $\text{Ln}^{3+}$  due to the lanthanide contraction phenomenon.<sup>19</sup>

In light of the literature precedent employing a two-step approach based on the preliminary formation of complexes with D-/L-phenylalanine, one can envision that the mechanism involved in the enantioenrichment at stake here using our

one-pot strategy involves the *in situ* formation of chiral assemblies of  $\text{Ln}(\text{III})$  cations with the enantiopure proline derivative that subsequently react with the btb ligand. It appeared of interest to employ another solvent, not comprising a carboxylic acid unit, to further extend our chiral induction strategy based on the use of enantiopure DES. In this context, the menthol:thymol (1:1)<sup>20</sup> DES was explored. Using this solvent and under the same conditions as detailed for the proline:thymol (1:7) DES, the synthesis of MIL-103(Tb) was explored. As confirmed by X-ray powder diffraction (Fig. 2 and Fig. ESI14†), the desired crystalline phase was obtained. The identity of MIL-103 was further supported by the FT-IR spectra corresponding to the ones obtained for the reference material as well as the MOFs obtained from the proline-based DES (Fig. ESI15 and ESI19†). It also shows the absence of residual menthol and/or thymol (Fig. ESI15†). TGA analysis under  $\text{N}_2$  demonstrated the same thermal stability of these materials as for the ones presented above (Table ESI1 and Fig. ESI16–18†). SEM micrographs of the materials prepared from the menthol–thymol (1:1) DES (Fig. ESI31–33†) also show a rod morphology, as when prepared from proline:thymol (1:7). The specific surface area calculated using the BET method based on  $\text{N}_2$  adsorption–desorption isotherms at 77 K (Table ESI1†) is in the same range (589–758  $\text{m}^2 \text{g}^{-1}$ ) as the ones for the MOFs prepared in proline–thymol (1:7) (Fig. 3).

Enantioenrichment was unambiguously demonstrated by diffuse-reflectance circular dichroism (Fig. 6) showing spectra with a signal at around 320 nm analogous, although weaker in intensity, to the ones collected for the MOFs prepared from the proline:thymol DES and the one reported for MOF enantioenriched using a two-step approach based on phenylalanine.<sup>15a</sup> This confirms that the emergence of the signal is derived from the chirality in the MOF and not any residual chiral component from the DES. However, it can be noted that

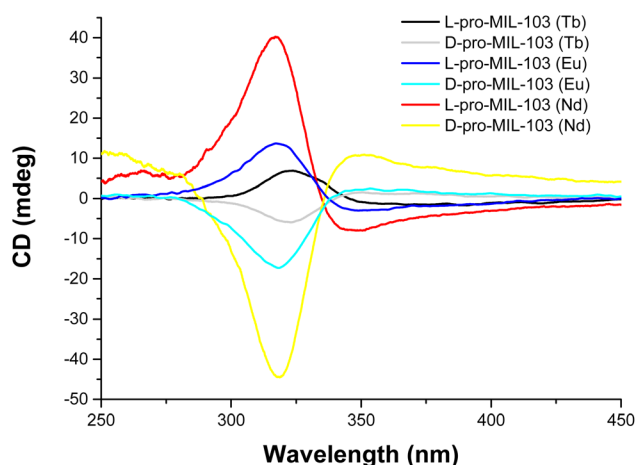


Fig. 5 Circular dichroism spectra of the MIL-103 MOF prepared in D-proline:thymol or L-proline:thymol, and DL-proline:thymol with different lanthanide cations: Tb, Eu, and Nd.

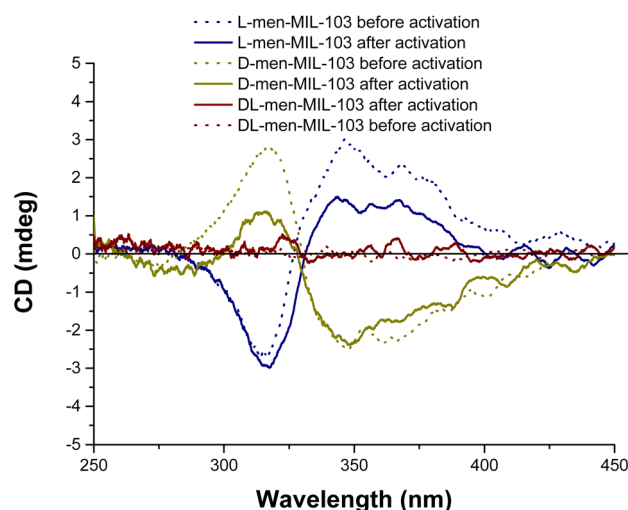


Fig. 6 Circular dichroism spectra of the MIL-103 MOF(Tb) prepared in D-menthol:thymol (1:1), L-menthol:thymol (1:1), and DL-menthol:thymol (1:1), before and after activation.





the activation process seems to impact the chirality more than that in the previous case. As expected, the material obtained from the racemic DL-menthol-thymol (1 : 1) DES did not lead to the appearance of a Cotton effect.

## Conclusion

In conclusion, the foregoing results demonstrate that enantiopure natural DESs can be employed as green media for the one-pot synthesis of enantioenriched MIL-103. The identity and purity of the MOFs were characterized using elemental analysis, FT-IR, TGA, X-ray powder diffraction and N<sub>2</sub> sorption-desorption isotherms. Chiral induction was assessed by diffuse-reflectance circular dichroism showing a Cotton effect for materials prepared from different enantiopure DESs, D- or L-proline : thymol (1 : 7) and D- or L-menthol-thymol (1 : 1). When using the racemic version of these solvents, such an effect could not be observed, consistent with the formation of a conglomerate, as for the reported reference material prepared from water : cyclohexanol (1 : 1). Since proline presents a structural analogy with phenylalanine previously reported to lead to the two-step enantioenrichment of this MOF,<sup>15a</sup> the chiral induction was first demonstrated using this solvent for the preparation of not only MIL-103(Tb) but also the Eu and Nd analogues, showing consistent Cotton effects for the three MOFs, depending on the chirality of the DES. In order to extend this strategy, a preliminary investigation was focused on the menthol-thymol (1 : 1) DES. While this solvent also led to the emergence of a Cotton effect, the process seems to be less efficient and straightforward using this DES and needs to be further optimised. Given the different nature of the chiral inductor (menthol vs. proline), a different mechanism, that remains to be determined, may be at stake for the enantioenrichment and responsible for this difference. As the CD spectrum of enantiopure MIL-103 could not be obtained, a quantitative estimation of the degree of enantioenrichment could not be assessed with this approach, preventing the determination of an enantiomeric ratio within the crystalline batches. However, it can be noted that mirror circular dichroism signals of opposite magnitude were observed depending on the chirality of the DES component. Future work will focus on the study of the impact of the chiral induction on the stereoselective activity of the MOFs such as for the cyanosilylation of aldehydes<sup>21</sup> or on their photophysical properties.

The one-pot strategy proposed herein may be considered as a green alternative to the conventional synthesis of CMOFs based on the preparation of chiral building units, an energy and time-demanding process and often requiring multiple steps and the use of diverse chemicals and reagents. Furthermore, in contrast with ionic liquids, previously reported as potential enantiopure solvents for such applications, DESs can be readily prepared from their natural affordable components, limiting waste generation and the need for purification steps. In addition to these advantages, the enantiopure natural DESs employed in this work can be

regarded as alternatives to solvents commonly used for solvothermal synthesis, such as DMF, DEF or NMP. The extension of this one-pot approach using enantiopure green solvents for the preparation of other MOFs as well as other types of porous materials such as COFs or zeolites is also envisioned to fully demonstrate its potential.

## Author contributions

Funding acquisition: S. A. B. and B. L.; experiments and data curation: R. A. M., A. F. and C. M.; investigation and interpretation of the results: R. A. M., C. M., S. A. B. and B. L.; writing of the original draft: R. A. M. and S. B.; revision of the manuscript and additional contributions: R. A. M. C. M., S. A. B. and B. L.

## Conflicts of interest

There are no conflicts to declare.

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