Volume 61
Number 17
28 February 2025
Pages 3411–3570

ChemComm

Chemical Communications

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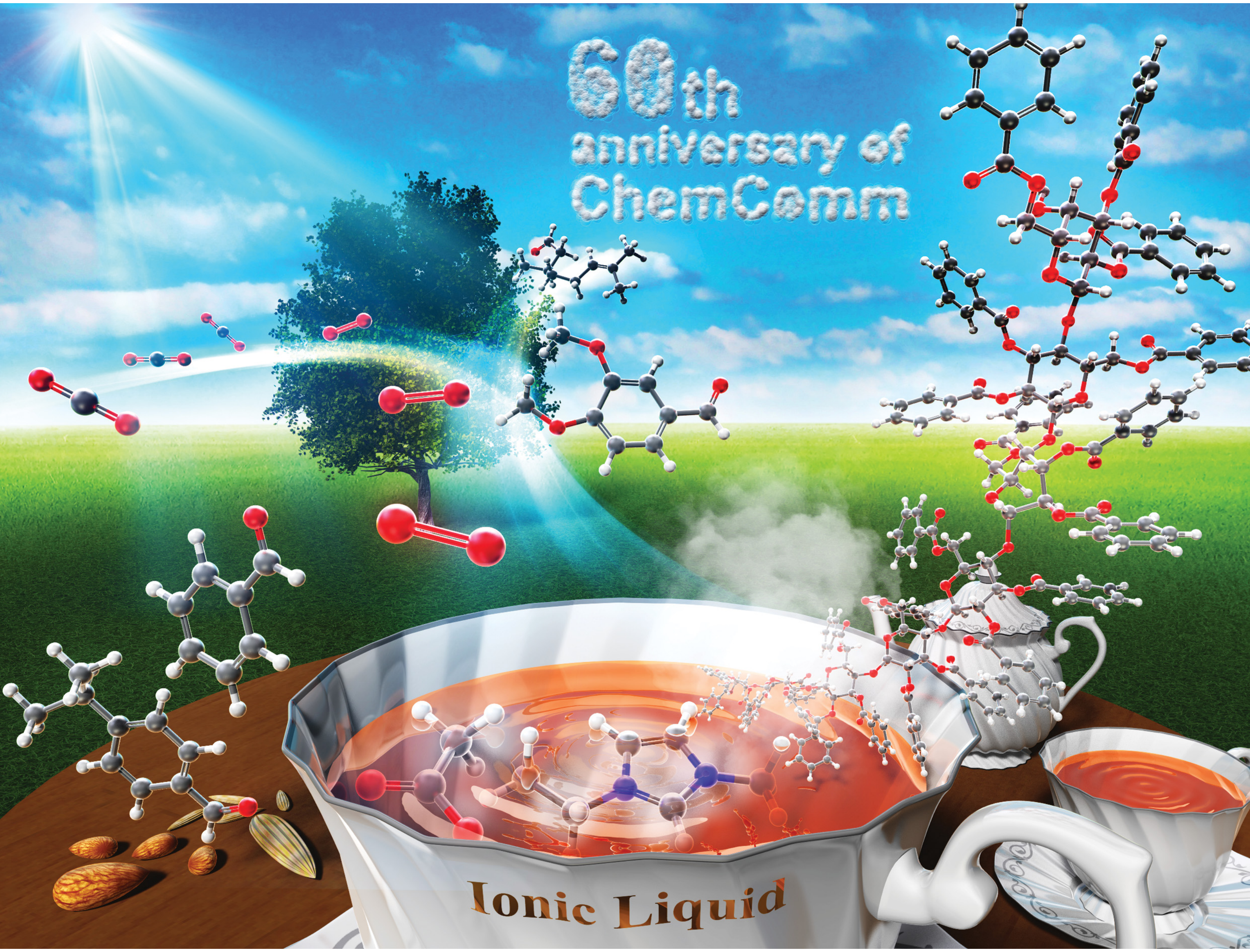

ISSN 1359-7345

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Cite this: *Chem. Commun.*, 2025, **61**, 3484

Received 14th September 2024,
Accepted 12th November 2024

DOI: 10.1039/d4cc04756g

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Fully bio-based cellulose ester synthesis from natural aldehydes *via* aerobic oxidation†

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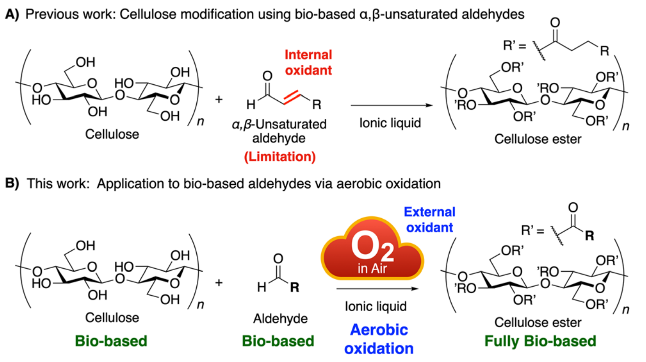
Kenji Takahashi *[a]

This study presents a novel synthetic method to synthesize fully bio-based cellulose esters from natural aldehydes in a multifunctional ionic liquid (as a solvent for cellulose and as an esterification and oxidation catalyst) in atmospheric oxygen. The aerobic oxidative esterification of cellulose with high atom economy proceeded under metal-free conditions without any additional catalysts or activators.

From the viewpoint of sustainability, switching from petroleum resources to bio-based materials is required, and several studies have been reported on the substitution of these resources with biofuels and bio-based materials.[1–4] Cellulose, a non-edible feedstock, is one of the most abundant carbohydrates present on Earth, and methods for its utilization are actively being investigated.[5,6] However, the hydrogen bond network formed by the hydroxyl group on cellulose greatly lowers its solubility in common solvents, making it difficult to modify the chemical structure, and this is one of the technical barriers to its application.[7–10] In 2002, Rogers *et al.* reported that ionic compounds with a melting point below 100 °C called "ionic liquids (ILs)" have unique properties that allow them to dissolve cellulose at high concentrations.[11–13] Thus, the cellulose modification research field, which was restricted to the use of special solvent systems such as *N,N*-dimethylacetamide (DMA)/LiCl and liquid ammonia,[14] has become active again.[15–21] Recently, the organocatalytic properties of imidazolium-type ILs have attracted considerable attention,[22–28] and our group has also reported the oxidative esterification of cellulose using bio-based α,β-unsaturated aldehyde in IL as solvent and catalyst (Scheme 1A).[29–31] In contrast to classical esterifications with carboxylic acids or their derivatives, this modification proceeds between cellulose and an aldehyde. An oxidant is necessary for the progress of the oxidative esterification reaction;[32] however, when using α,β-unsaturated aldehydes, such as cinnamaldehyde contained in cinnamon bark,[33] the desired cellulose ester can be obtained using the C═C bond as an internal oxidant and without any additional oxidants.[34,35] This green synthesis method shows utility compared with other bio-based polymer syntheses, because it can directly obtain a fully bio-based polymer capable of contributing to carbon neutrality.[36] However, the scope of the reaction is limited to α,β-unsaturated aldehydes.

Various natural aldehydes other than α,β-unsaturated aldehyde, such as the cumin seed-derived cumin aldehyde,[37] exist. To utilize the abundant array of natural aldehydes, expanding the aldehyde scope of the reaction is necessary. Meanwhile, in the presence of an *N*-heterocyclic carbene (NHC), the oxidative esterification reaction of aldehydes without internal oxidants is known to proceed with external oxidants, such as manganese dioxide, azobenzene, and molecular oxygen.[38–42] However, cellulose is insoluble in common organic solvents used in general synthetic chemistry, making the direct application of the reported reaction systems to cellulose conversion difficult.[21,29] Therefore, our approach using ILs as a solvent and catalyst is considered to be effective for oxidative esterification reactions using external oxidants. There is an inexhaustive supply of molecular oxygen in the



Scheme 1 Schematic illustration of the oxidative esterification of cellulose in an ionic liquid using α,β-unsaturated aldehydes (A) and general aldehydes *via* aerobic oxidation ((B), this work).

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† Electronic supplementary information (ESI) available: Synthetic procedures and characterization of cellulose esters. See DOI: https://doi.org/10.1039/d4cc04756g

atmosphere, and it is therefore an ideal green oxidant because the resulting byproduct is water.

In this study, we investigated the oxidative esterification of cellulose with aldehyde in an IL using molecular oxygen as the external oxidant and revealed that a fully bio-based cellulose ester can be obtained by only dissolving cellulose and a natural aldehyde in an IL in atmospheric oxygen under metal-free and mild conditions (Scheme 1B).

For our initial attempt, we used 1-ethyl-3-methylimidazolium acetate (EmimOAc) (Fig. 1) as the IL and benzaldehyde (**1**), known as the primary component of bitter almond oil,[43] as the acyl donor (Table 1, entry 1). Equimolar amounts of benzaldehyde the hydroxyl groups on the cellulose ([**1**]/[ROH] = 1/1, molar ratio) were added to a solution of cellulose dissolved in EmimOAc/dimethylsulfoxide (DMSO) = 1/20 (molar ratio), and the mixture was heated at 60 °C under an O_2 (balloon) atmosphere for 24 h. DMSO was added to reduce the viscosity of the solution and to improve the catalytic activity of the ionic liquid.[44] This reaction solution was in a homogenous state from start to end, indicating that EmimOAc functioned as a solvent of cellulose in this system. After the reaction, the resulting polymer was recovered as a white fibrous solid from the reaction mixture by reprecipitation in MeOH. Infrared (IR) measurements of the obtained cellulose derivatives revealed an absorption band at 1711 cm^{-1} corresponding to the C=O stretching derived from the aromatic ester group. The presence of this band demonstrated the progress of the cellulose esterification reaction with benzaldehyde (**1**) (Fig. S1, ESI†).

In the proton nuclear magnetic resonance (^1H NMR) spectrum of the obtained product in DMSO-d_6, proton peaks at 2.5–5.8 ppm derived from the cellulose backbone and those at 7.0–8.2 ppm derived from the benzaldehyde aromatic ring were observed (Fig. S2a, ESI†). Subsequently, the degree of substitution (DS) of the resulting product was determined. To increase the solubility of the resulting cellulose benzoate in acetone-d_6, the remaining hydroxyl group of the product was additionally modified with acetic acid using condensation reagents to prepare per-acetylated cellulose acetate benzoate. The ^1H NMR spectra of the resulting per-acetylated cellulose benzoate gave the integral ratio between the cellulose backbone and aromatic ring, and the DS value of the desired benzoate group (DS_{main}) was estimated to be 0.55 (Fig. S2b, ESI†). However, the proton peaks of the acetyl group derived from the EmimOAc anion were observed at approximately 1.8–2.2 ppm (Fig. S2a, ESI†). As previously reported, this is attributed to the undesired side reaction found in the esterification of cellulose in EmimOAc.[45–47] As evidenced by these ^1H NMR measurements, the DS value of the undesired acetyl group (DS_{side}) was estimated to be *ca.* 0.01. These results show that a fully bio-based cellulose ester could be directly synthesized from a saturated aldehyde under oxygen in an IL system without any additional catalysts and activators.

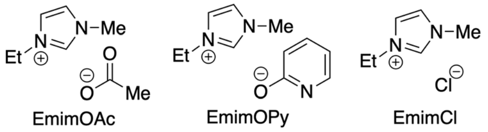
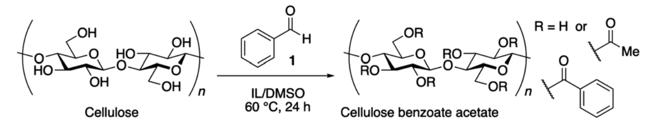


Fig. 1 Chemical structures of the imidazolium salts.

Table 1 Effect of the reaction conditions on the oxidative esterification of cellulose with benzaldehyde (**1**)[a]



Entry	IL	Atmosphere	DS_{main}
1	EmimOAc	O_2	0.55
2[d]	EmimOAc	O_2	0.43
3	EmimOAc	Air	0.97
4	EmimOAc	Ar	Trace[b]
5	EmimCl	Air	n.d.[b]
6	EmimOPy	Air	1.38–1.75[c]
7[e]	EmimOPy	Air	1.31

[a] Reaction conditions: [ROH]/[**1**]/[IL]/[DMSO] = 1/1/1/20 (molar ratio), 24 h, 60 °C, air atmosphere. [b] Based on the absorption band at around 1711 cm^{-1} corresponding to C=O stretch in the IR spectrum (Fig. S1, ESI). [c] Results of three experiments. [d] DMF was employed instead of DMSO. [e] [ROH]/[**1**] = 1/2 (molar ratio).

The effect of reaction conditions was examined (Table 1). *N*,*N*-Dimethylformamide (DMF) as a co-solvent afforded a comparable result (DS_{main} = 0.43) to those of using DMSO (Table 1, entry 2). Similar to pure oxygen gas, atmospheric oxygen facilitated the reaction, and the DS value of the cellulose benzoate was slightly improved (DS_{main} = 0.97) (Table 1, entry 3). To evaluate the influence of oxygen on this reaction, a control experiment was carried out using inert argon (Ar) gas. Here, almost no C=O band was observed at approximately 1711 cm^{-1} in the resulting product (Fig. S1, ESI†); this result strongly implied that this reaction required molecular oxygen to proceed (Table 1, entry 4). When Emim chloride (EmimCl) was employed as the IL the reaction mixture became homogenous; however, the absorption band at approximately 1711 cm^{-1}, which indicated ester stretching and demonstrated that the reaction had progressed successfully, was not observed in the resulting product due to the lack of anion basicity (Table 1, entry 5). Recently, we have reported that Emim 2-pyridonate (EmimOPy), which has basic a non-carboxylate-type anion, works as an effective IL for the oxidative esterification of cellulose to prevent the undesired introduction of anion-derived ester groups and achieve high DS values.[30,31] When the reaction was carried out using EmimOPy, the desired oxidative esterification proceeded, and a distinct increase in the DS value was confirmed (DS_{main} = 1.38–1.75; as the results of three experiments) (Table 1, entry 6). The range of fluctuation for the DS was around ±6% of the median (1.57), comparable to the deviation in ordinary reactions. No clear increase in DS value was observed when the amount of aldehyde was increased ([ROH]/[**1**] = 1/2 (molar ratio)) (DS_{main} = 1.31) (Table 1, entry 7).

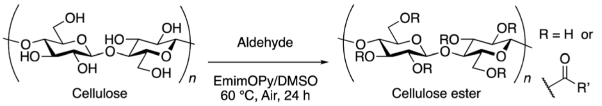
We investigated the kinetics of this oxidative esterification of cellulose *via* aerobic oxidation. Fig. S3 (ESI†) shows the time-dependent change of the DS value of cellulose benzoate under the conditions of entry 6 in Table 1. The time for the DS value to reach a plateau in EmimOPy was found to be 24 h.

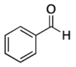
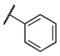
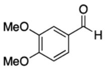
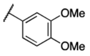
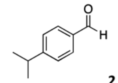
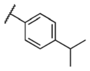
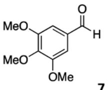
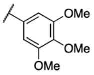
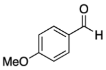
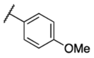
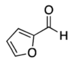
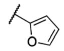
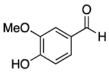
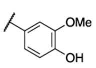
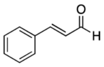
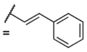
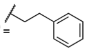
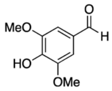
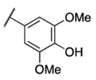
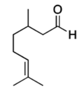
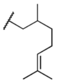
The scope of the bio-based aldehydes tolerated by the optimized conditions (Table 1, entry 6) was investigated, and the results are shown in Table 2. Cumin seed-derived cuminaldehyde (**2**) and anise seed-derived anisaldehyde (**3**), which have isopropyl and methoxy groups on their aromatic rings, afforded the corresponding cellulose esters without any undesired introduction of the anion-derived ester, and their DS values were determined to be 1.33 (**2**) and 1.69 (**3**), respectively (Table 2, entries 2 and 3). In contrast, in the case of vanillin (**4**) and syringaldehyde (**5**), which are bio-based and lignin-derived compounds obtained through biorefining,[48] the resulting polymers did not show any IR band absorption at approximately 1710 cm^{-1} corresponding to C=O group (Fig. S4, ESI†), indicating that no progress in oxidative esterification took place (Table 2, entries 4 and 5). However, inexpensive and commercially available methylated vanillin "veratraldehyde" (**6**) and 3,4,5-trimethoxybenzaldehyde (**7**), known as a bio-based odorant and an industrial intermediate for pharmaceuticals, afforded the corresponding cellulose esters with moderate DS values of 1.48 (Table 2, entry 6) and 1.22 (Table 2, entry 7), respectively. These results suggested that the phenolic hydroxy group on the aromatic aldehyde was responsible for the failure of reaction in the cases of **4** and **5**. For furfural (**8**), which can be obtained from hemicellulose through biorefining,[49] the product showed an IR band at approximately 1700 cm^{-1} derived from the ester group (Fig. S4, ESI†). However, the product was almost unrecoverable from the soluble parts because of its affinity for solutions containing ILs, despite screening the precipitation conditions, and the DS value after per-acetylation (Table 2, entry 8) was difficult to determine. Previously, we reported that the oxidative esterification using cinnamon-derived cinnamaldehyde (**9**) proceeded using the C=C bond as the internal oxidant even in an Ar atmosphere.[29] When the experiments were conducted under atmospheric oxygen, no peaks were observed in the 5.5–6.5 ppm region corresponding to a C=C group, indicating that the internal redox system was faster than the aerobic oxidation process and that the reduced cellulose phenylpropionate (DS = 0.79) without a C=C group had been obtained (Table 2, entry 9). A bio-based aliphatic aldehyde "citronellal" (**10**) obtained from eucalyptus and citronella, afforded the desired cellulose ester, albeit with a low DS value (0.10) (Table 2, entry 10). The obtained cellulose esters (DS > 1.0) showed a number-average molecular weight (M_n) of 3.7–4.6 $\times 10^4$, which is reasonable for the starting cellulose substrate (Table S1, ESI†). It was confirmed that these cellulose esters had sufficient solubility for wet processing using organic solvents (Table S2, ESI†). During the course of these studies, no clear evidence of oxidative degradation of the products could be detected from any IR, NMR, and size-exclusion chromatography (SEC) measurements.

Based on previous studies,[29,30,46] a plausible mechanism for the oxidative esterification of cellulose was tentatively suggested and shown in Fig. 2. Imidazolium salts bearing anions with sufficient basicity form Breslow intermediate **A** in concert with the aldehydes.[25,30] Electron-rich **A** is oxidized by molecular oxygen to form acylimidazolium intermediate **B**, followed by a reaction with an alcohol to give the desired ester (main pathway).[23,32,41,42] Meanwhile, for the ILs with a carboxylate anion, such as EmimOAc, a mixed acid anhydride **C** is generated from **B** (side pathway), some of which is converted to the undesired ester (acetyl group) detected in Fig. S2a (ESI†).[22,29,45–47]

In conclusion, a new green cellulose modification method has been developed to obtain a fully bio-based plastic to meet carbon neutrality goals. This is achieved by merely dissolving natural cellulose and saturated aldehydes in an IL system under

Table 2 Scope of the oxidative esterification of cellulose *via* aerobic oxidation[a]



Entry	Aldehyde	Product	DS	Entry	Aldehyde	Product	DS
1	 **1**	R' = 	1.38–1.75[b]	6	 **6**	R' = 	1.48
2	 **2**	R' = 	1.33	7	 **7**	R' = 	1.22
3	 **3**	R' = 	1.69	8	 **8**	R' = 	–[d]
4	 **4**	R' = 	n.d.[c]	9	 **9**	R' =  R' = 	n.d. 0.79
5	 **5**	R' = 	n.d.[c]	10	 **10**	R' = 	0.10

[a] Reaction conditions: [ROH]/[aldehyde]/[EmimOPy]/[DMSO] = 1/1/1/20 (molar ratio); 24 h; 60 °C under air. [b] Results of three experiments. [c] Based on the absorption band at around 1710 cm^{-1} corresponding to C=O stretch in the IR spectrum (Fig. S4, ESI). [d] The product was almost unrecoverable from the soluble parts.

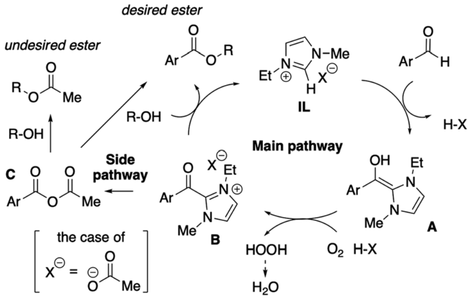


Fig. 2 Plausible mechanism of the oxidative esterification of cellulose in ionic liquids *via* aerobic oxidation.

atmospheric oxygen, without any additional catalysts or activators. ILs, typically EmimOPy, performed a triple role (as solvent, esterification catalyst, and aerobic oxidation catalyst), yielding highly substituted cellulose esters (DS = *ca.* 1.8 at the maximum) under metal-free reaction condition with high atom economy. By using molecular oxygen as an external oxidant, various bio-based aldehydes, such as aromatic and even aliphatic aldehydes, can be utilized in the cellulose ester synthesis. Further optimization of the ILs for high reactivity and an even wider aldehyde scope, such as vanillin, and a mechanistic study of this oxidative esterification *via* aerobic oxidation in ILs are in progress in our laboratory.

S. B. W. K. is thankful for the kind support of the Indonesian Endowment Fund for Education (LPDP), Ministry of Finance; Directorate for Resources, Ministry of Education Culture, Research, and Technology, Republic of Indonesia. This work was predominantly funded by a Kanazawa University frontier science and innovation cooperation young investigator grant (D. H.), the Shorai Foundation for Science and Technology (D. H.), the Japan Science and Technology Agency (JST) (grant number JPMJPF2102) and the Japan Society for the Promotion of Science (JSPS) KAKENHI (grant numbers 18H02253 and 22H02404).

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare no competing financial interest.

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