# Supporting information for:

# Sustainable functionalization of cellulose and starch with diallyl carbonate in ionic liquids

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- 1) IR-Spectra of modified cellulose and starch (including optimization studies)
- 2) NMR data of modified starch
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- 5) TGA data of modified cellulose and starch
- 6) Tensile strength measurements of modified cellulose
- 7) NMR data of recovered DAC and BMIMCI

1) IR-Spectra of modified cellulose and starch (including optimization studies)



**Fig. S1** ATR-IR spectra of filter paper and modified filter paper with diallyl carbonate (DAC) (DS: ~1.3) in BMIMCI/DMSO solvent mixture (18 h, 4 eq. DAC, 80 °C, 10% (w/w) DMSO & 2% (w/w) cellulose concentration). Spectra were normalized to the intensity of the glycopyranose oxygen absorption at around 1050 cm<sup>-1</sup>.



**Fig. S2** ATR-IR spectra of maize starch and modified maize starch with DAC (DS: ~1.2) in BMIMCI/DMSO solvent mixture (18 h, 4 eq. DAC, 80 °C, 10% (w/w) DMSO & 2% (w/w) starch concentration). Spectra were normalized to the intensity of the glycopyranose oxygen absorption at around 1015 cm<sup>-1</sup>.



**Fig. S3** ATR-IR spectra of carbonyl peak intensities (left) of modified filter paper with DAC in different ionic liquids, 1-butyl-3methylimidazolium chloride (BMIMCI), 1-ethyl-3-methylimidazolium acetate (EMIMOAc) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF<sub>4</sub>) (18 h, 3 eq. DAC, 80 °C, 10% (w/w) DMSO & 2% (w/w) cellulose concentration) and ATR-IR spectra of carbonyl peak intensities (right) of modified filter paper with different molar ratios of DAC in BMIMCI/DMSO solvent mixture (18 h, 80 °C, 10% (w/w) DMSO & 2% (w/w) cellulose concentration). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm<sup>-1</sup>.



**Fig. S4** ATR-IR spectra of carbonyl peak intensities (left) of modified filter paper with DAC in BMIMCI/DMSO solvent mixture using different catalysts (18 h, 4 eq. DAC, 80 °C, 10 mol% of catalyst, 10% (w/w) DMSO & 2% (w/w) cellulose concentration) and ATR-IR spectra of carbonyl peak intensities (right) of modified filter paper with DAC in BMIMCI/DMSO solvent mixture at different reaction temperatures (18 h, 4 eq. DAC, 10% (w/w) DMSO & 2% (w/w) cellulose concentration). Spectra were normalized to the intensity of the glycopyranose oxygen absorption at around 1050 cm<sup>-1</sup>.

#### 2) NMR data of modified starch



Fig. S5 <sup>1</sup>H NMR (left) and <sup>13</sup>C NMR (right) of modified starch with DAC.

#### 3) NMR data of phosphorylated, modified cellulose and starch



Fig. S6 <sup>31</sup>P NMR of modified filter paper with DAC.



Fig. S7 <sup>31</sup>P NMR of modified maize starch with DAC.



4)	GPC	data	of	modified	cellulose	and	starch
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Product <sup>a</sup>	M <sub>w</sub> [kDa]	M <sub>n</sub> [kDa] <sup>b</sup>	Ð
Filter paper	78	40	1.93
CC7	349	82	4.20
CC8	67	15	4.32

<sup>a</sup>Reaction conditions: 18 h, 3eq. DAC, BIMIMCI/DMSO solvent mixture (10% (w/w)) DMSO & 2% (w/w) cellulose concentration). 4All GPC measurements were carried out relative to poly(methyl methacrylate) calibration in DMAc/LiBr (1% w/w)

Fig. S8 GPC data of unmodified filter paper and modified filter paper with DAC at different temperatures.



Product <sup>a</sup>	M <sub>n</sub> [kDa] <sup>b</sup>	M <sub>w</sub> [kDa]	Ð
SC1	84	523	6.21
SC2	66	256	3.88
SC3	12	27	2.19

<sup>a</sup>Reaction conditions: 18 h, 3eq. DAC, BIMIMC//DMSO solvent mixture (10% (w/w) DMSO & 2% (w/w) starch concentration).
<sup>b</sup>All GPC measurements were carried out relative to poly(methyl methacrylate) calibration in DMAc/LiBr (1% w/w).

Fig. S9 GPC data of modified maize starch with DAC at different temperatures.



#### 5) TGA data of modified cellulose and starch

Fig. S10 TGA data of unmodified filter paper, modified filter paper with DAC (CC5) and thiol-ene product of cellulose allyl carbonate (CC5T).



Fig. S11 TGA data of unmodified maize starch and modified maize starch with DAC.

## 6) Tensile strength measurement of modified cellulose



Fig. S12 Tensile strength measurement of modified filter paper with DAC (DS: ~1.3).

## 7) NMR data of recovered DAC and BMIMCI



Fig. S13 <sup>1</sup>H NMR of recovered DAC.



Fig. S14 <sup>1</sup>H NMR of recovered BMIMCI.