Supporting Information

Formic acid-mediated liquefaction of chitin

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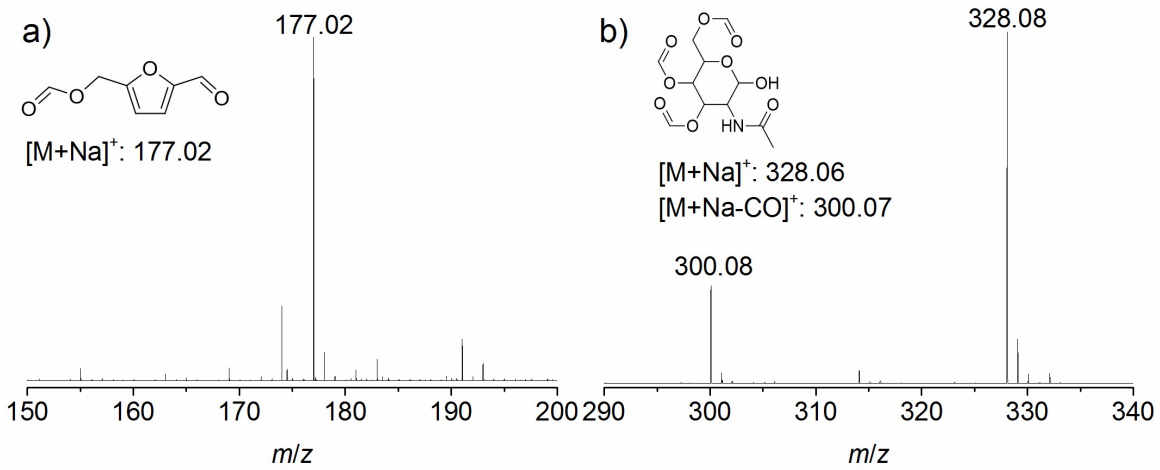
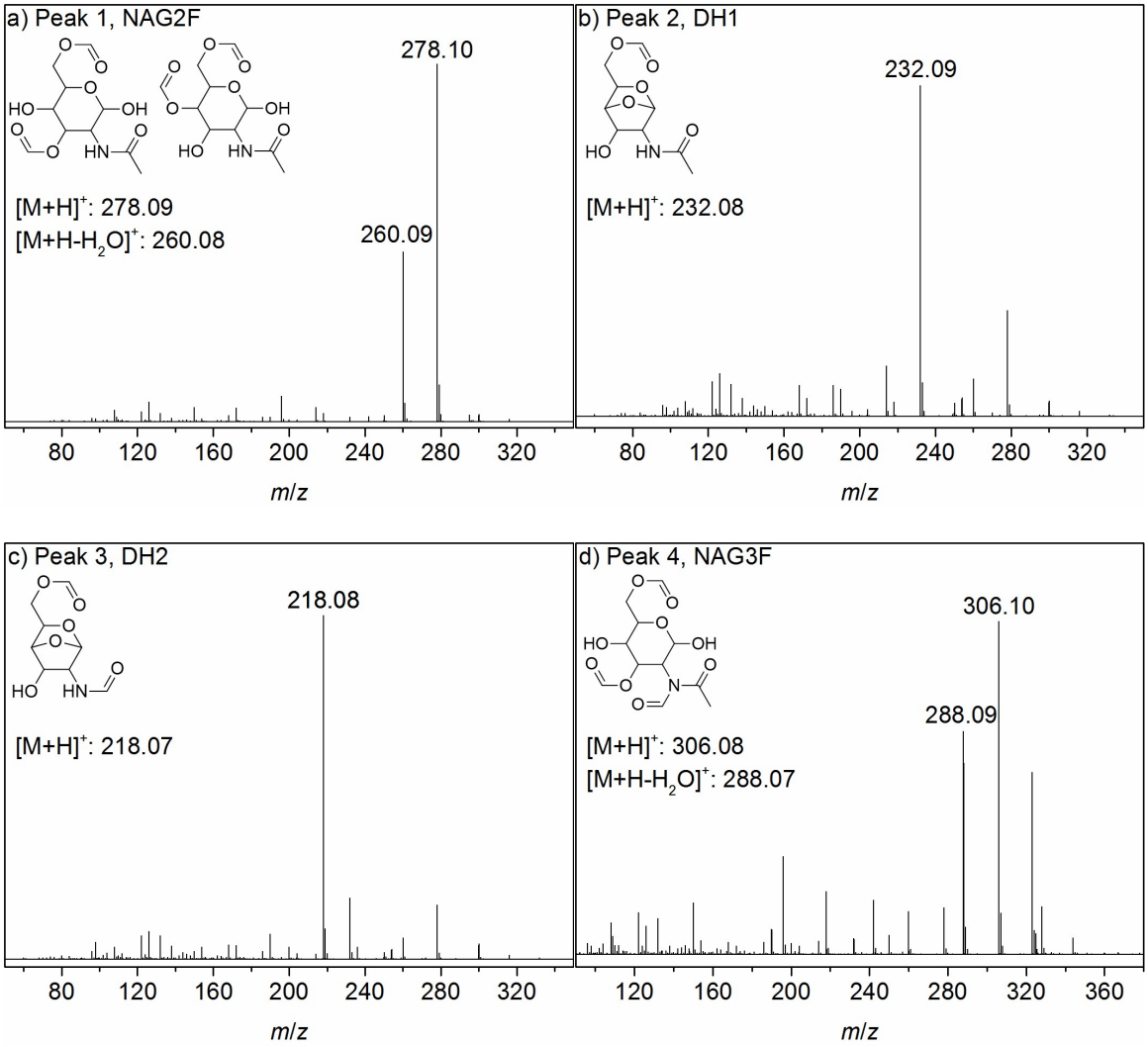


Fig. S1 ESI-MS spectra for a) FMF and b) NAG3F.



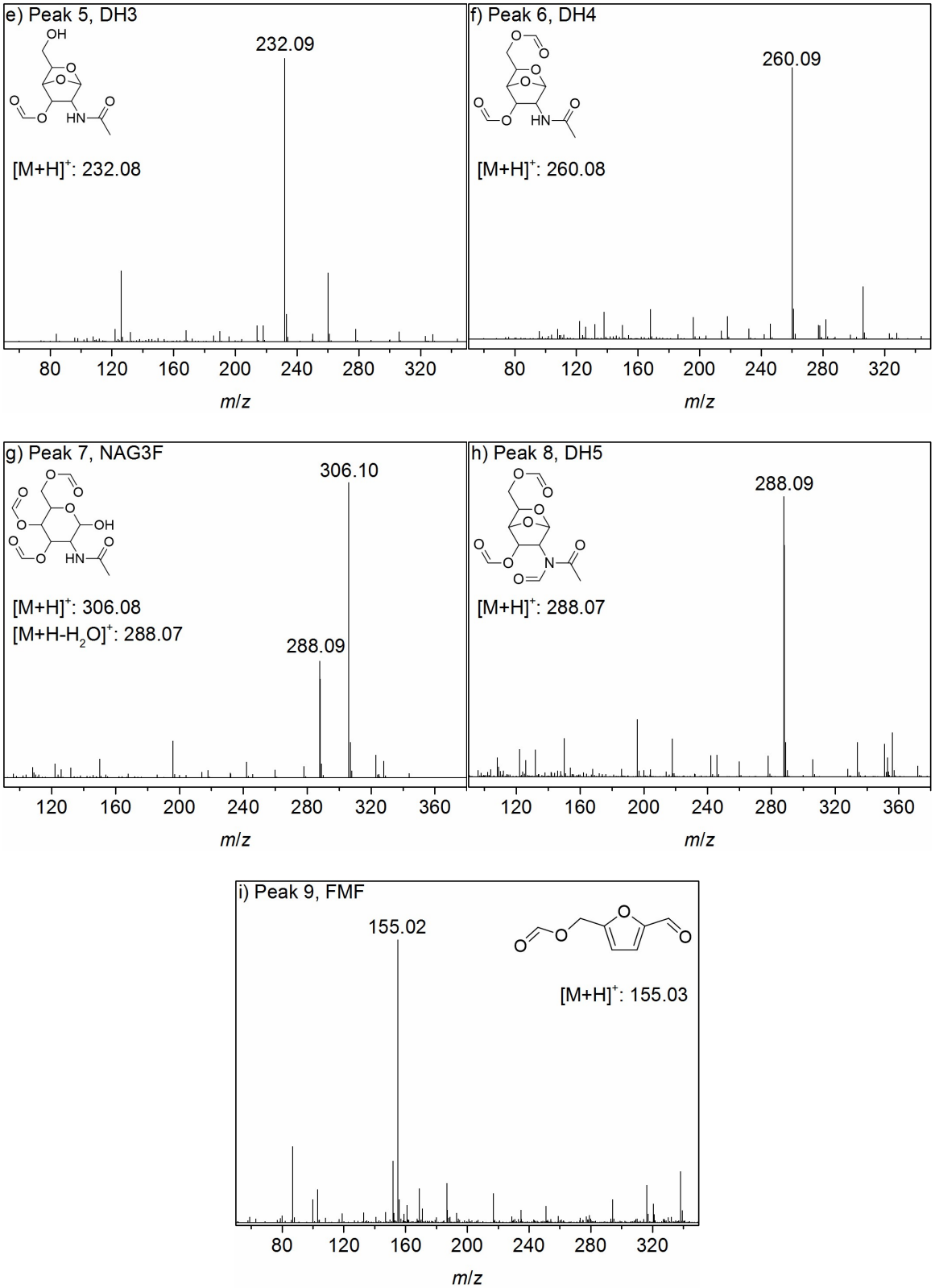


Fig. S2 MS spectrum of peaks selected from LC-MS analysis.

Quantification method

HPLC calibration curves were obtained from purified FMF and NAG3F as standard samples (Fig. S3), with which the response factors for FMF at 280 nm and NAG3F at 210 nm were obtained. Since the formate and acetate groups has maximum absorption at ca. 210 nm, the response factors for other NAGFs and DHs were estimated from that for NAG3F. For example, since NAG3F has 3 formate groups and 1 acetate group whereas NAG2F has 2 formate groups and 1 acetate groups, the response factor for NAG2F was estimated as 3/4 of response factor for NAG3F.

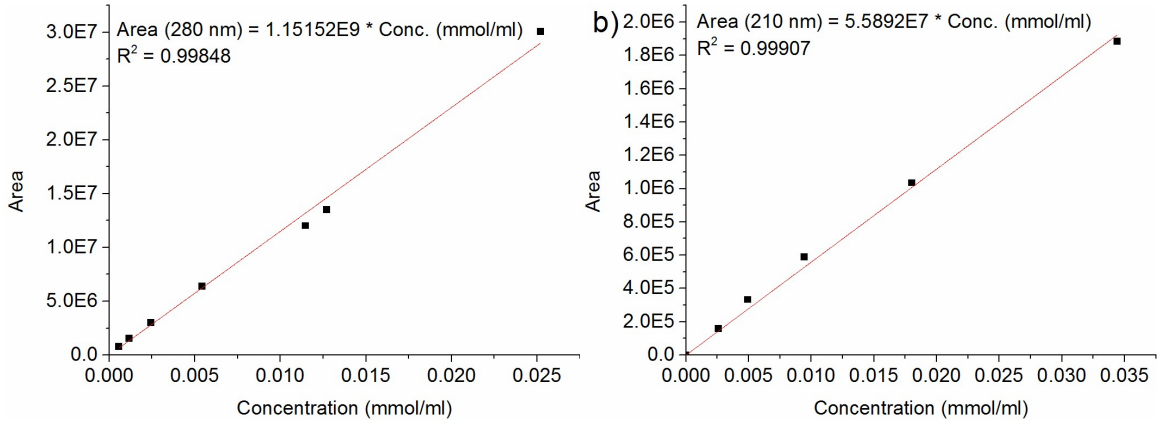


Fig. S3 HPLC calibration curves for a) FMF at 280 nm and b) NAG3F at 210 nm.

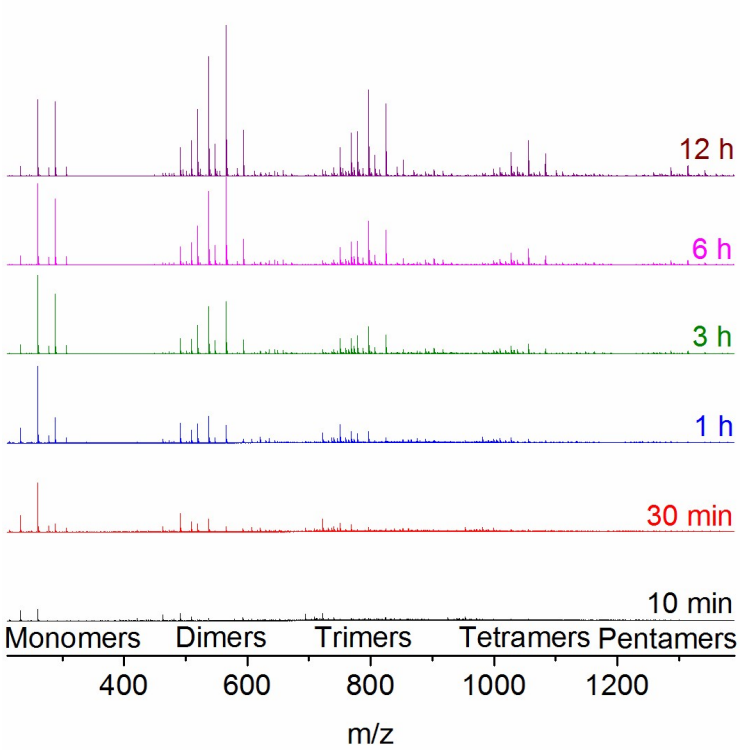


Fig. S4 ESI-MS spectra of liquefaction products after different reaction time. Reaction conditions: 50 mg BM-chitin, 5 ml formic acid, 80 °C, 12 h.

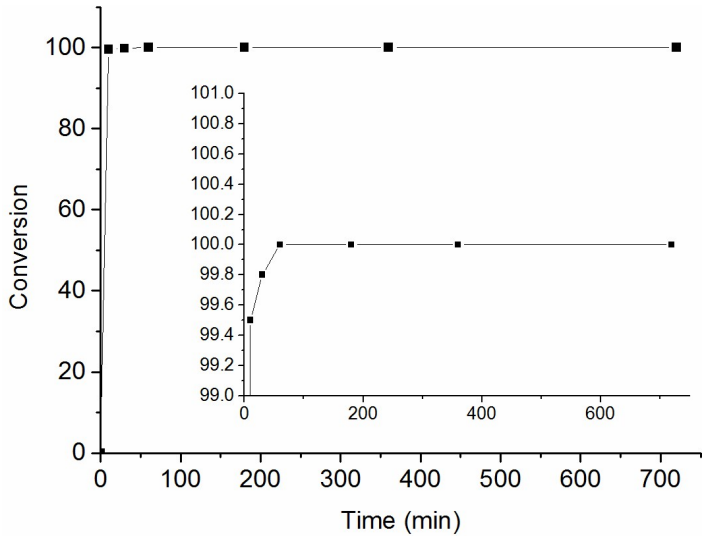


Fig. S5 Conversion of BM-chitin with different reaction times. Inset: enlarged Fig. at around conversion close to 100%. Reaction conditions: 50 mg BM-chitin, 5 ml formic acid, 80 °C.

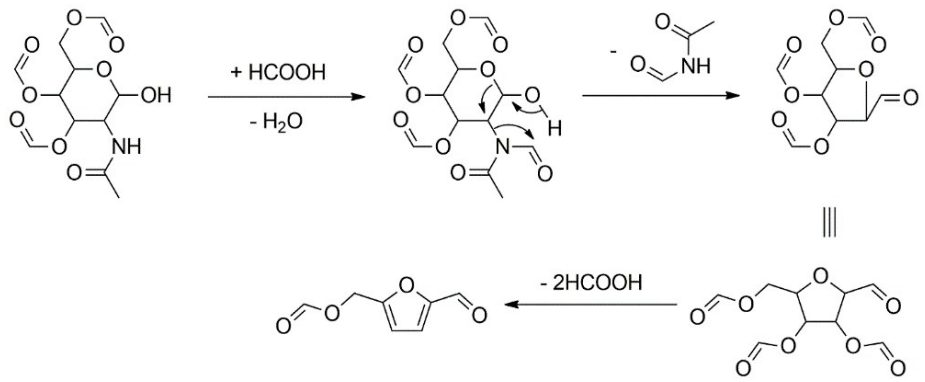


Fig. S6 Proposed "2,5-dehydration" mechanism for FMF formation from NAG3F.

Table S1. Formic acid mediated liquefaction efficiency with different BM-chitin loadings.

Entry	BM-chitin (mg)[a]	Residue (mg)	Liquefaction efficiency (%)
1	50.0	0	100
2	100.0	0.6	99.4
3	200.0	0.8	99.6
4	500.0	4.4	99.1
5	1000.0	21.0	97.9

[a] Reaction conditions: 5 ml formic acid, 80 °C, 12 h.

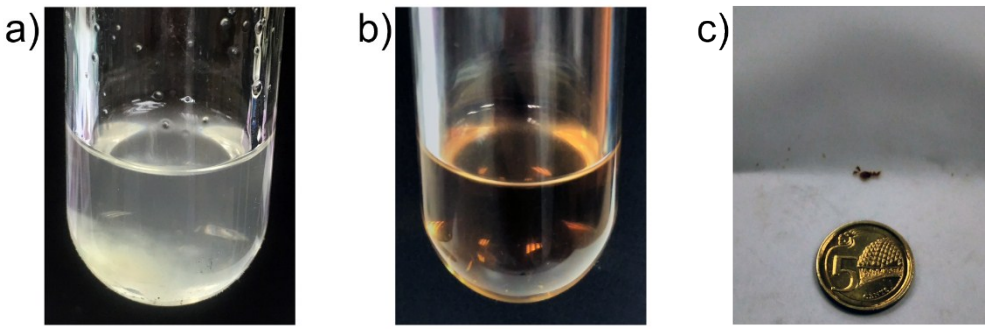


Fig. S7 a) BM-chitin in formic acid before liquefaction. b) Formic acid solution after liquefaction. c) Solid residue (reference: 5 cent Singapore coin, O.D. = 16.75 mm). Reaction conditions: 100 mg BM-chitin, 5 ml formic acid, 80 °C, 12 h.

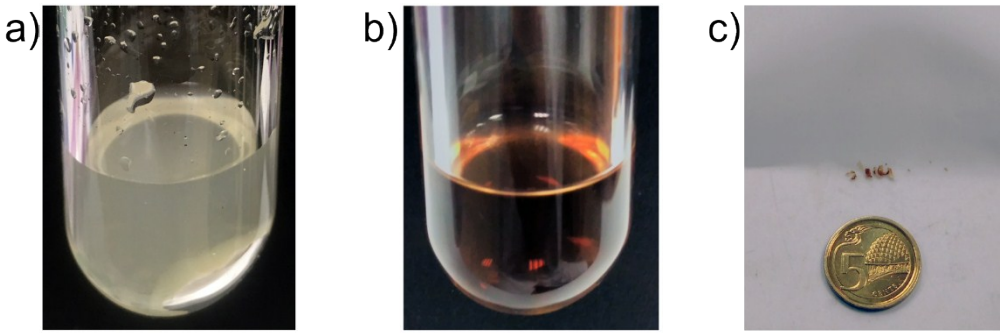


Fig. S8 a) BM-chitin in formic acid before liquefaction. b) Formic acid solution after liquefaction. c) Solid residue (reference: 5 cent Singapore coin, O.D. = 16.75 mm). Reaction conditions: 200 mg BM-chitin, 5 ml formic acid, 80 °C, 12 h.

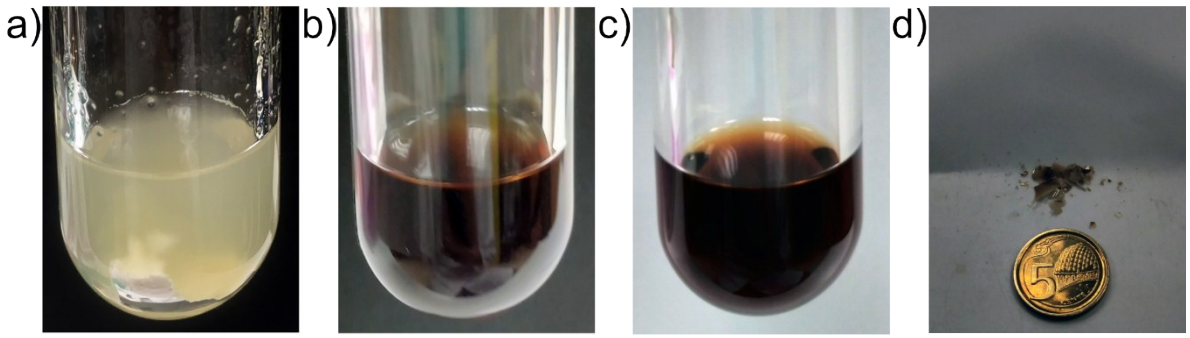


Fig. S9 a) BM-chitin in formic acid before liquefaction. b) Formic acid solution after liquefaction against black background. c) Formic acid solution after liquefaction against white background. d) Solid residue (reference: 5 cent Singapore coin, O.D. = 16.75 mm). Reaction conditions: 500 mg BM-chitin, 5 ml formic acid, 80 °C, 12 h.

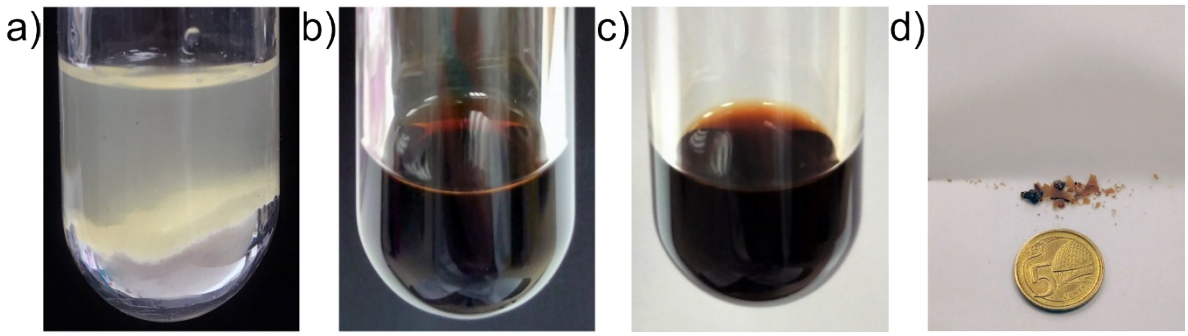


Fig. S10 a) BM-chitin in formic acid before liquefaction. b) Formic acid solution after liquefaction against black background. c) Formic acid solution after liquefaction against white background. d) Solid residue (reference: 5 cent Singapore coin, O.D. = 16.75 mm). Reaction conditions: 1000 mg BM-chitin, 5 ml formic acid, 80 °C, 12 h.

Fractionation of the shrimp shell

The shrimp shell powder was firstly oven dried at 105°C for 12 h, where the weight loss was regarded as moisture. Then the dried powder was treated with 2 wt% NaOH solution at 90 °C for 2 h for deproteination. After adequate washing and drying, the demineralization was conducted in 2.5 % HCl at room temperature for 1 h. The leftover solid was chitin. The procedure was done three times in parallel, from which, the shrimp shell was determined to contain 16.9 wt% moisture, 31.8 wt% protein, 22.9 wt% $CaCO_3$, and 28.3 wt% chitin.

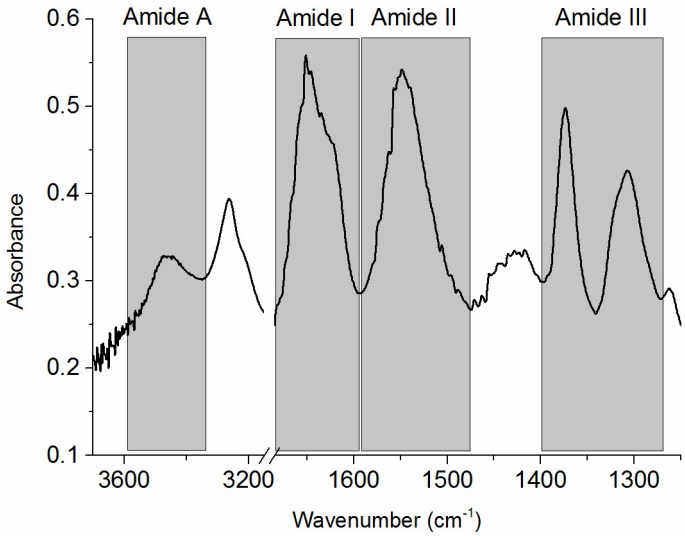


Fig. S11 ATR-FTIR spectrum of solid residue after shrimp shell liquefaction. Reaction conditions: 50 mg shrimp shell powder, 5 ml formic acid, 80 °C, 12 h.

Note: The band at ca. 3500 cm^{-1} can be assigned as Amide A band due to the stretching of N-H bond in peptides. The bands at 1650 cm^{-1} and 1550 cm^{-1} are ascribed to the vibrations of the C=O, C-N, and N-H bonds in peptides, namely Amide I and Amide II, respectively. The bands at 1400~1300 cm^{-1} are from the hydrogen bonds and side chains.[1] The FTIR spectrum is in good accordance with the characteristic features of protein, indicating the solid residue in shrimp shell liquefaction is mainly protein.

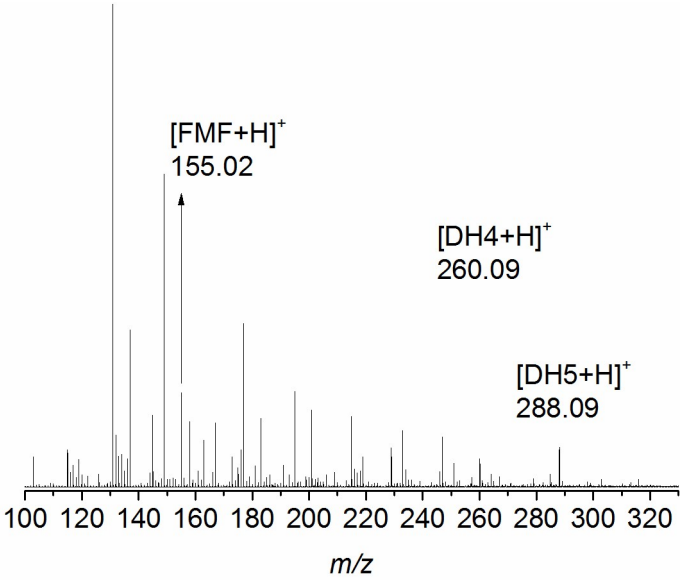


Fig. S12 ESI-MS spectrum of shrimp shell liquefaction products. Reaction conditions: 50 mg shrimp shell powder, 5 ml formic acid, 80 °C, 12 h.

Reference

1. G. Zandomeneghi, M. R. H. Krebs, M. G. McCammon and M. Fändrich, *Protein Sci.*, 2004, **13**, 3314-3321.