# Breaking the symmetry of dibenzoxazines: a paradigm to tailor the design of bio-based thermosets

L. Puchot, <sup>a,b</sup> P. Verge\*, <sup>a</sup> T. Fouquet, <sup>a</sup> C. Vancaeyzeele, <sup>b</sup> F. Vidal, <sup>b</sup> and Y. Habibi\*, <sup>a</sup>

<sup>a</sup> Luxembourg Institute of Science and Technology (LIST), 5 avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg. <sup>b</sup> Laboratoire de Physicochimie des Polymères et des Interfaces (LPPI – EA 2528), I-Mat, Université de Cergy-Pontoise. 5, mail Gay-Lussac, 95031 Cergy-Pontoise, France.

Correspondance to: <u>\* Youssef Habibi (Youssef.Habibi@list.lu</u>); Pierre Verge (Pierre.Verge@list.lu)

# SUPPORTING INFORMATION

Content	Page
Results and discussion	2
Characterization by HRMS analysis of the di-vanillin Bz monomer	2
Characterization by HRMS analysis of the Vani-Card Bz monomer	3
Characterization by HRMS analysis of the di-cardanol Bz monomer	4

Di-benzoxazine monomers were found to strongly react during the timeframe of mass analysis through ion/molecules reactions upon the addition of water and the subsequent release of formaldehyde from the protonated compound.[1] Since air humidity encountered during the preparation undoubtedly accounts for this ion/molecule reaction, their occurrences have not been avoided despite the use of a solvent-free sample preparation.

Surprisingly, additional peaks are also readily observed at m/z 557 + congeners, further assigned to deprotonated  $[M-H]^+$  species. Several compounds have already been found to yield  $[M-H]^+$  "abnormal" pseudo-molecular ions with electrospray ionization (ESI) [2] and atmospheric pressure photoionization (APPI) [1].To the best of our knowledge, this is nevertheless the first report of such  $[M-H]^+$  ions for the benzoxazine class with MALDI-MS. Additionally, di-Bz were also found to strongly react during the timeframe of the mass analysis through ion/molecules reactions, with the detection of  $[M+H+H_2O-CH_2O]^+$  ions at m/z 547 + congeners for Vani-Card, formed upon the addition of water and the subsequent release of formaldehyde from the protonated compound. Since air humidity encountered during the preparation undoubtedly accounts for this ion/molecule reaction, their occurrences have not been avoided despite the use of a solvent-free sample preparation.



#### 1. Characterization of the di-vanillin Bz monomer

**Figure S1** HRMS analysis of di-vanillin Bz monomer **a**) Zoom of the experimental product peaks **b**) Theoretical mass of the expected product



Figure S2 MS/MS analysis of di-vanillin Bz monomer

## 2. Characterization of the Vani-Card Bz monomer



**Figure S3** HRMS analysis of Vani-Card Bz monomer **a**) Zoom of the experimental product peaks **b**) Theoretical mass of the expected product

Page 3 of 5 - Correspondence to: youssef.habibi@list.lu; pierre.verge@list.lu

### 3. Characterization of the di-cardanol Bz monomer



Figure S4 HRMS analysis of di-cardanol Bz monomer a) Zoom of the experimental product peaks b) Theoretical mass of the expected product



Figure S5 MS/MS analysis of di-cardanol Bz monomer

Page 4 of 5 - Correspondence to: youssef.habibi@list.lu; pierre.verge@list.lu

- 1. Sioud, S., et al., *The formation of [M-H]+ ions in N-alkyl-substituted thieno[3,4-c]-pyrrole-4,6-dione derivatives during atmospheric pressure photoionization mass spectrometry.* Rapid Commun. Mass Spectrom., 2014. **28**(Copyright (C) 2015 American Chemical Society (ACS). All Rights Reserved.): p. 2389-2397.
- 2. Guo, Z.-Q., et al., [M-H]+ ions in 3-alkyl substituted indoles detected by electrospray mass spectrometry. Int. J. Mass Spectrom., 2014. **361**(Copyright (C) 2015 American Chemical Society (ACS). All Rights Reserved.): p. 54-58.