SUPPORTING INFORMATION

Alkali Cation Chelation in Cold β -O-4 Tetralignol Complexes

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I. Modifications to AB Sciex API 2000 RF Power Supplies

To improve the mass accuracy and resolution of the q2 and q3 linear ion traps, our previously used home-made RF power supplies were replaced with a modified power supply from a decommissioned AB Sciex API 2000 mass spectrometer. Numerous electrical modifications were made to the QPS exciter module in order to bypass its interlock and to interface the supply with our instrument control software. The coils of the supply's two tank circuits were retapped such that resonance was achieved at the exciters existing drive frequencies of 650kHz (q2, Extrel quadrupole rod set) and 1MHz (q3, Sciex quadrupole rod set). In order to maximize the peak voltage output of the supply, the dipolar excitation toroid necessary for MSAE was moved into the vacuum chamber so that the cable capacitance running from the coil output to the feedthrough could be minimized. The high degree of RF stability afforded by the power supply allows for broadband mass isolations in q2 that are stable indefinitely, a critical parameter in obtaining long UV scans (*i.e.*, 3 hour long scans for IR-UV hole burning to obtain conformation specific UV spectra). Furthermore, the supply greatly improved the mass accuracy [two point calibration based on YGGFL-H⁺ ($m/z = 556$) and YGGFL-Na⁺ ($m/z = 578$) accurate to within $\Delta m/z = \pm \frac{1}{2}$ between $m/z = 397$ and $m/z = 1,111$] and resolution [$\frac{m}{\Delta m} \approx 3,000$ at $m/z = 1,111$ for YGGFL₂H⁺]

of our analysis LIT. This has allowed us to obtain low signal UVPD mass spectra by MSAE with isotopic resolution and it has been possible to distinguish loss channels that differ by a few daltons.

II. Synthesis of the G-Type β -O-4 Tetralignol Compound

Scheme S.1. Synthetic Route for lignin tetramer **S8**

A convergent synthesis of lignin tetrameric precursor **S4** was used (Scheme S1).¹ The starting material **S3** was prepared according to the procedure by Mariano and coworkers.² A previous study used a stepwise synthesis, which had longer synthetic steps. The condensation of two dimeric units **S2** and **S10** gave **S4** in good yield. **S2** (the anti-isomer) was synthesized according to a literature procedure.³ The remaining steps were similar as the previous trimer synthesis.³ Compound **S4** was obtained as an inseparable mixture of two diastereomers (anti/syn ratio 4:1 according to NMR), which was then reduced with NaBH_4 at room temperature to yield **S5** in excellent yield. The anti-isomer **S6** was isolated after the 1,3-diol was protected with acetonide group. **S7** was obtained after hydrogenation in good yield. The tetrameric compound **S8** was obtained after deprotection under acidic condition.

Compound S3

To a solution of **S1** (4.8 g, 13.3 mmol) in dry acetone (120 ml), methyl α -bromoacetate (3.0 g, 20.0 mmol, 1.9 ml) and anhydrous K_2CO_3 (2.7 g, 20.0 mmol) were added at room temperature. The mixture was heated at reflux overnight, then filtered, washed with AcOEt and the filtrate was concentrated to give yellowish oil, which was purified by chromatography (hexane/AcOEt 2:1) to give colorless syrup (5.0 g, 11.6 mmol, yield 88 %).

1H NMR (400 MHz, $CDCl_3$) δ 7.09 – 7.00 (m, 2H), 6.91 – 6.66 (m, 4H), 6.47 (dd, J = 8.0, 1.4 Hz, 1H), 4.91 (d, J = 8.7 Hz, 1H), 4.64 (s, 2H), 4.27 – 4.10 (m, 2H), 4.06 – 3.94 (m, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 1.63 (s, 3H), 1.50 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 214.4, 169.3, 150.3, 149.2, 146.8, 133.6, 122.7, 120.7, 119.5, 117.4, 113.9, 112.0, 111.2, 99.4, 74.3, 66.4, 62.8, 55.7, 55.6, 52.1, 28.4, 19.6

HRMS(ESI) Calcd. for $C_{23}H_{28}O_8Na$: 455.1682 $[M+Na^+]$, found: 455.1681.

Compound S4

n-Butyllithium (1.5 ml of a 2.5 M solution in hexanes, 3.5 mmol) was added at 0 °C to a solution of diisopropylamine (0.49 ml, 3.5 mmol) in dry THF (15 ml). After 20 min at 0 °C, a solution of **S3** (1 g, 2.3 mmol) in dry THF (5 ml) was added at -78°C followed by, after 10 min, a solution of **S2** (1.1 g, 2.3 mmol) in dry THF (5 ml). After 1h at -78 °C, saturated aqueous NH_4Cl (30 ml) was added and the mixture extracted with AcOEt (3 $\times$ 20 ml). The combined extracts were dried over Na_2SO_4 , filtered and concentrated to give viscous oil consisting of a mixture of the two possible diastereomeric (syn/anti 4:1) compounds. (1.6 g, 1.7 mmol, yield after purification 73%, hexane:AcOEt 1:1).

^1H NMR (400 MHz, CDCl_3) δ 7.46-7.40 (m, 5H), 7.04-6.66 (m, 11H), 6.47-6.41 (m, 2H), 5.11 (s, 2H), 5.05 – 4.97 (m, 1H), 4.94 – 4.82 (m, 2H), 4.66 – 4.56 (m, 1H), 4.13 (m, 4H), 4.04 – 3.92 (m, 2H), 3.84 (s, 1H), 3.76 (s, 1H), 3.71 (s, 6H), 3.60 (s, 3H), 1.62 (s, 6H), 1.49 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 169.6, 150.1, 149.4, 147.9, 146.8, 137.2, 135.3, 133.7, 132.4, 128.5, 127.7, 127.2, 122.8, 120.7, 120.0, 119.6, 119.0, 118.6, 117.3, 116.9, 113.8, 112.1, 111.6, 111.1, 110.7, 99.4, 83.9, 74.4, 73.5, 70.9, 62.8, 55.9, 55.7, 52.0, 28.4, 19.7.

HRMS (ESI) Calcd. for $\text{C}_{51}\text{H}_{58}\text{O}_{15}\text{Na}$: 933.3673 $[\text{M}+\text{Na}^+]$, found: 933.3733.

Compound S5

NaBH_4 (0.47 g, 12.4 mmol) was added at room temperature portionwise in 3 h to a solution of **S4** (1.6g, 1.7 mmol) in THF: H_2O 3:1 (40 ml). After 24 h at room temperature under stirring, 50ml H_2O was added and the solution was extracted with AcOEt. The combined organic extracts were dried over Na_2SO_4 , filtered and the solvent was evaporated to give compound **S12** as white foam (1.4 g, 1.6 mol, yield 90%) sufficiently pure to be used in the following step.

^1H NMR (400 MHz, CDCl_3) δ 7.40-7.28 (m, 5H), 7.08-6.60 (m, 10H), 6.49-6.41 (m, 3H), 5.10 (s, 2H), 4.96 – 4.91 (m, 1H), 4.90 – 4.85 (m, 1H), 4.85 – 4.81 (m, 1H), 4.17-4.10 (m, 4H), 4.03-3.99 (m, 4H), 3.84 (s, 3H), 3.80 (s, 3H), 3.73 (s, 3H), 3.70 (s, 3H), 3.58 – 3.46 (m, 1H), 1.64 (s, 3H), 1.63 (s, 3H), 1.52 (s, 3H), 1.50 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 151.2, 150.3, 150.2, 149.3, 147.8, 146.8, 146.3, 137.1, 135.4, 134.4, 132.2, 128.4, 127.7, 127.1, 122.7, 120.6, 120.4, 119.7, 118.1, 117.3, 117.2, 113.7, 112.0, 111.4, 111.3, 111.1, 109.8, 99.4, 87.3, 74.5, 72.2, 70.8, 62.7, 60.4, 55.6, 28.4, 19.6.

HRMS (ESI) Calcd. for $\text{C}_{50}\text{H}_{58}\text{O}_{14}\text{Na}$: 905.3724 $[\text{M}+\text{Na}^+]$, found: 905.3780.

Compound S6

Camphorsulfonic acid (28 mg, 0.11 mmol) was added to a solution of **S5** (1.24 g, 1.4 mmol) and 2, 2-Dimethoxypropane (DMP) (0.86 ml, 7 mmol) in dry acetone (25 ml). The mixture was stirred overnight. After the completion of the reaction, 20 ml of saturated aqueous NaHCO₃ was added. The solution was extracted with AcOEt (3 x 20ml). The organic phase was combined, washed with brine, dried over Na₂SO₄, filtered and concentrated to give a mixture of diastereomers. The anti-isomer **S6** could be isolated by chromatography (hexane:AcOEt 3:1) to give a colorless oil (0.8 g, 0.87 mmol, yield 62%).

¹H NMR (400 MHz, CDCl₃) δ 7.42-7.28 (m, 5H), 7.07-6.63 (m, 10H), 6.47-6.42 (m, 3H), 5.12 (s, 2H), 4.92 – 4.88 (m, 1H), 4.85 (d, *J* = 8.5 Hz, 1H), 4.14-4.07 (m, 6H), 4.01-3.95 (m, 3H), 3.85 (s, 3H), 3.70 (s, 3H), 3.68 (s, 6H), 1.63 (s, 3H), 1.62 (s, 3H), 1.61 (s, 3H), 1.51 (s, 3H), 1.50 (s, 6H).
¹³C NMR (100 MHz, CDCl₃) δ 150.3, 150.0, 149.4, 147.8, 146.7, 146.6, 137.2, 133.9, 133.7, 132.4, 128.4, 127.6, 127.1, 122.7, 120.6, 119.6, 119.3, 117.2, 116.6, 116.5, 113.8, 112.0, 111.4, 111.1, 99.4, 74.3, 74.0, 70.9, 62.7, 55.8, 55.6, 28.4, 19.6.

HRMS (ESI) Calcd. for C₅₃H₆₂O₁₄Na: 945.4037 [M+Na⁺], found: 945.4098.

Compound S7

A solution of **S6** (0.8 g, 0.87 mmol) in EtOH (10 ml) was added to 10% Pd/C (80 mg) and hydrogenated at atmospheric pressure and 20 °C for 5 h. The solution was filtered over Celite, concentrated *in vacuo* to give **S7** as colorless syrup (0.59 g, 0.71mmol, 82%), which was used for the next reaction step without purification.

¹H NMR (400 MHz, CDCl₃) δ 6.99-6.66 (m, 10H), 6.46-6.34 (m, 3H), 5.85 (brs, 1H), 4.99-4.84 (m, 3H), 4.12-4.06 (m, 6H), 4.01 – 3.94 (m, 3H), 3.75 – 3.61 (m, 13H), 1.62 (s, 3H), 1.59 (s, 6H), 1.50 (s, 3H), 1.48 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 150.3, 149.9, 146.8, 146.3, 145.4, 133.6, 131.0, 122.6, 120.6, 120.3, 119.8, 119.5, 117.3, 116.7, 116.3, 114.1, 112.0, 111.3, 109.9, 99.3, 74.46, 62.7, 55.6, 28.4, 19.6.

HRMS (ESI) Calcd. for $\text{C}_{46}\text{H}_{56}\text{O}_{14}\text{Na}$: 855.3568 $[\text{M}+\text{Na}^+]$, found: 855.3613.

Compound S8

To a solution of **S7** (0.2 g, 0.24 mmol) in acetone– H_2O 1:1 (4 ml), PPTS (30 mg, 0.12 mmol) was added at room temperature and the mixture was heated at reflux for 20 h. Acetone was removed *in vacuo* to give an oil which was purified by flash chromatography on silica gel (CH_2Cl_2 : EtOH 20:1) to give pure **S8** (140 mg, 0.2 mmol, yield 82%).

^1H NMR (400 MHz, Acetone- d_6) δ 7.68 (brs, 1H), 7.10 (s, 3H), 6.96-6.76 (m, 10H), 4.90 (m, 4H), 4.77 (brs, 1H), 4.31 (s, 3H), 4.06 (brs, 1H), 3.85-3.81 (m, 4H), 3.76 (s, 12H), 3.71-3.68 (m, 2H), 3.32 (brs, 4H).

^{13}C NMR (100 MHz, Acetone- d_6) δ 151.6, 151.2, 148.8, 148.0, 146.5, 137.0, 134.1, 123.2, 121.9, 120.3, 119.0, 118.3, 115.2, 113.4, 112.3, 111.4, 86.0, 73.5, 61.6, 56.2

HRMS (ESI) Calcd. for $\text{C}_{37}\text{H}_{43}\text{O}_{14}$: 711.2653 $[\text{M}-\text{H}^-]$, found: 711.2668.

III. IR-UV Hole Burning Example

Conformation-specific UV spectra were obtained by IR-UV hole-burning spectroscopy. As described in the experimental section, fixed resonant IR excitation of a particular conformer selectively warms this conformer and broadens its UV spectrum. When the spectrum taken with the IR laser turned on is subtracted from spectrum taken with the IR laser turned off, a conformation-specific UV spectrum is revealed because only the peaks that are associated with a particular conformer dip. The raw spectra prior to subtraction that were used to obtain the UV spectrum of the major conformer of the Li^+ adduct (manuscript Fig. 12) are shown in Fig. S.1

Fig. S.1. UV action spectrum of the Li⁺ cationized G-type β -O-4 lignin tetramer measured with the IR laser on resonance (3475 cm⁻¹) with conformer A (red trace) and with the IR laser turned off (black trace).

IV. Zero-Point Corrected DFT Energies and Global Minimum Structures

The 100 lowest energy conformers of the Li^+ , Na^+ , and K^+ adducts from a Monte Carlo Multiple Minimum (MCMM) search using the MacroModel⁴ implementation of the Merck Molecular Force Field (MMFFs)⁵ were reoptimized at the M05-2X/6-31G* level of theory.⁶ The relative force field and DFT single point energies along with a description of each structure is provided in the supporting Excel file (Lowest100DFT.xls). These structures were ordered according to their single point energies and the twenty lowest-energy structures were re-optimized at the M05-2X/6-31+G* level of theory with a tight optimization convergence criteria and an ultrafine grid (int=ultrafine). Harmonic-level vibrational frequency calculations were also performed on these low energy structures. In Tables S.1, S.2, and S.3 we report the relative force field, single-point DFT, and zero point corrected DFT energies of the twenty lowest energy conformers of the Li^+ , Na^+ , and K^+ species, respectively.

These tables also include descriptions of the metal cation binding pockets and H-bonding structural motifs in each of the low energy structures. The “number of $\text{M}^+\cdots\text{OH}/\text{M}^+\cdots\text{OR}/\pi//\text{M}^+\cdots\text{OH}\cdots\text{OH}/\text{M}^+\cdots\text{OH}\cdots\text{OR}$ interactions” column counts interactions between the metal cation and oxygen atoms in each distinct chemical environment. Specifically, $\text{M}^+\cdots\text{OH}$ and $\text{M}^+\cdots\text{OR}$ interactions involve OH(R) groups that bind to the metal cation and are not H-bond donors, while $\text{M}^+\cdots\text{OH}\cdots\text{OH}$ and $\text{M}^+\cdots\text{OH}\cdots\text{OR}$ interactions consist of $\text{M}^+\cdots\text{OH}$ interactions with subsequent H-bond donation to an OH group or an OR group, respectively. These H-bonds are labelled “s” and “w” to denote “strong” vs. “weak”, respectively, which was visually assessed for each structure based on the H-bond length (shorter implies stronger) and the O-H $\cdots$ O angle (closer to 180° implies stronger). The $/\pi$ is included when there is contact between the M^+ cation and one of the π clouds. The total coordination number of the M^+ cation can be obtained by adding the

numbers between the / marks. We also indicate secondary H-bonds that are formed when the H-bond acceptor of an $M^+ \cdots OH \cdots OH$ interaction functions as an H-bond donor to an additional $OH(R)$ group ($M^+ \cdots OH \cdots OH \cdots OR$). The “Pocket” column indicates which O atoms bind to the M^+ ion. These O atoms are either covalently bound to one of the aromatic rings (R) or are part of one of the β -O-4 linkage (L). The numbering (Rn , Lm) begins at the end of the oligomer containing the guaiacol moiety. The “hinge type” describes the direction of the H-bond that occurs within the L2 linkage. In particular, $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \alpha$ imply a C_6 H-bond from the α OH group to the γ OH group and *vice versa*, whereas γ C_5 implies a C_5 H-bond between the γ OH group and the aryl ether group on R3. The subscript in $\alpha \rightarrow \gamma_r$ denotes a rotamer of the alpha OH group that forms a less direct H-bond.

In Fig. S.2, the relative DFT (M05-2X/6-31G*) vs. MMFFs energies are plotted in the case of the Li^+ species. The poor correlation between these energies highlights the need to perform many DFT calculations in order to more fully explore the potential energy surface. Although 100 DFT geometry optimizations were performed for each set of structures, it was possible to find low energy conformers by manually altering structures from the ones found by the Monte Carlo search. For example, the conformer labeled “11a” in Table S.1 is 6.02 $kJ \cdot mol^{-1}$ above the lowest energy structure (conformer 2). Fig. S.3 shows a comparison between the structures of conformer 11, 11 Altered (11a), and 2 (the global minimum) in the case of the Li^+ species. In Fig. S.3 $M^+ \cdots OH \cdots OH$, $M^+ \cdots OH \cdots OR$, and $M^+ \cdots OH \cdots OH \cdots OR$ H-bonds are also circled to clarify the nomenclature used in Tables S.1-S.3. Key angles and H-bond distances pertaining to these strong interactions ($OH \cdots O$ distances $< 2 \text{ \AA}$ and $OH \cdots O$ angles close to 180°) are also labeled in the case of the assigned structure (11a). The calculated global minima structures of the Li^+ , Na^+ , and K^+ adducts are illustrated in Fig. S.4.

TABLE S.1: Calculated Energies of G-Type β -O-4 Tetramer Li^+ Adducts Obtained from an MCOMM Search

DFT Order	Force Field Order	MMFFs Energy (kJ·mol ⁻¹)	DFT Single Point Energy (kJ·mol ⁻¹)	Zero-Point Corrected (kJ·mol ⁻¹)	Number of Li ⁺ ...OH/Li ⁺ ...OR/ π // Li ⁺ ...OH...OH/Li ⁺ ...OH...OR Interactions ^b	Li ⁺ ...OH...O H...OR Present y/n	Pocket ^c	Hinge Type ^d
1	2	3.10	0	0	0/2//1s/2s	y	R1,L3,R4	$\alpha \rightarrow \gamma$
2	4	6.73	2.60	1.10	1/2//0/2s	n	L1,L3,R4	$\alpha \rightarrow \gamma$
3	48	20.3	4.70	3.93	1/2/ π //1s/0	y	L1,R2,L3	$\alpha \rightarrow \gamma$
4	37	19.0	7.03	4.84	1/2//1s/1s	n	L1,L3,R4	γ C5
5	12	13.0	5.15	4.85	2/1//0/2s	n	L1,R2,L3	free
6	63	22.4	6.90	4.98	2/2//0/1s	n	L1,L3,R4	$\alpha \rightarrow \gamma$
7	72	24.1	6.91	5.06	1/2/ π //0/1w,1s	n	L1,R2,L3	$\gamma \rightarrow \alpha$
8	80	24.9	9.01	6.02	2/2//0/1s	n	L1,L3,R4	$\alpha \rightarrow \gamma$
9	11a ^a	---	5.68	6.02	0/2//1s/1s,1w	n	L1,R2,L3	$\alpha \rightarrow \gamma$
10	22	16.3	9.64	6.37	1/2//1w/1s	n	L1,L3,R4	γ C5
11	3	4.28	10.4	9.15	0/2//1s/2s	y	R1,L3,R4	$\alpha \rightarrow \gamma$
12	39	19.2	11.9	10.1	1/2//1w/1s	n	L1,L3,R4	$\alpha \rightarrow \gamma$
13	9	10.4	10.8	10.1	0/2//1s/1s,1w	n	L1,R2,L3	$\alpha \rightarrow \gamma_r$
14	35	18.4	11.3	10.2	1/2//1s/1s	n	L1,L3,R4	$\alpha \rightarrow \gamma$
15	6	8.69	11.8	10.4	0/2//1s/1s,1w	n	L1,R2,L3	γ C5
16	42	19.6	11.1	10.4	1/2//1s/1s	n	L1,L3,R4	$\gamma \rightarrow \alpha$
17	29	17.6	13.9	12.6	2/1//0/1s,1w	n	L1,R2,L3	γ C5
18	10	10.8	13.2	12.8	1/2//1s/1s	n	L1,L3,R4	$\gamma \rightarrow \alpha$
19	11	11.8	14.4	12.8	0/2//1s/1s,1w	n	L1,R2,L3	free
20	94	26.1	18.1	16.8	0/2//1s/2w	n	L1,R2,L3	$\alpha \rightarrow \gamma_r$
21	81	24.9	21.0	20.6	0/2//1s,1w/1w	n	L1,R2,L3	$\alpha \rightarrow \gamma_r$

^a 11a is the conformer that best fits the experimental IR spectrum of the major conformer and was derived from conformer 11 by forming a C₆ H-bond between the α and γ OH groups. ^b s = strong, w = weak. The nomenclature “/ π ” denotes a Li⁺... π interactions. ^c The three linkages are labeled L1, L2, and L3 with respect to the guaiacol (g) end of the tetramer and the three rings are labeled R1, R2, and R3. ^d The C₆ hydrogen bond at the hinge position is denoted $\alpha \rightarrow \gamma$, or $\gamma \rightarrow \alpha$ to represent the relative orientation of the α and γ OH groups. The subscript “r” is an abbreviation for “rotamer” and applies to the L2 γ group. The γ C₅ H-bond is between the L2 γ OH and aryl ether group of R3.

TABLE S.2: Calculated Energies of G-Type β -O-4 Tetramer Na^+ Adducts Obtained from an MCMM Search

DFT Order	Force Field Order	MMFFs Energy (kJ·mol ⁻¹)	DFT Single Point Energy (kJ·mol ⁻¹)	Zero-Point Corrected (kJ·mol ⁻¹)	Number of $\text{Na}^+\cdots\text{OH}/\text{Na}^+\cdots\text{OR}/\pi//\text{Na}^+\cdots\text{OH}\cdots\text{OH}/\text{Na}^+\cdots\text{OH}\cdots\text{OR}$ Interactions ^c	$\text{Na}^+\cdots\text{OH}\cdots\text{O}$ $\text{H}\cdots\text{OR}$ Present y/n	Pocket ^d	Hinge Type ^e
1	10	8.51	0	0	1/2/ π //1w/1w	y	L1,R2,L3	γ C5
2	4	6.06	1.99	0.651	1/2/ π //1w/1w	y	L1,R2,L3	γ C5
3	1	0	4.94	3.62	1/2/ π //0/1s,1w	n	L1,R2,L3	$\alpha \rightarrow \gamma$
4 ^a	---	---	2.97	4.82	0/2/ π //1w/1s,1w	y	L1,L3,R4	free
5	61	18.0	9.31	5.71	1/2//0/1s,2w	n	L1,R2,L3	free
6	12	9.19	5.13	5.72	0/2//1s/1s,1w	n	L1,R2,L3	$\alpha \rightarrow \gamma_r$
7	8	7.58	8.80	5.74	1/2/ π //0/2w	n	L1,R2,L3	free
8 ^b	2	5.62	6.38	6.20	0/2//1s/1s,1w	n	L1,R2,L3	$\alpha \rightarrow \gamma$
9	6	6.88	7.53	7.43	0/2//1s/1s,1w	n	L1,R2,L3	$\alpha \rightarrow \gamma$
10	15	9.54	7.34	7.54	0/2//1s/1s,1w	n	L1,R2,L3	$\alpha \rightarrow \gamma_r$
11	14	9.50	11.0	7.98	1/2/ π //1w/1w	n	L1,R2,L3	γ C5
12	19	11.1	11.2	8.18	1/2/ π //1w/1w	y	L1,R2,L3	$\alpha \rightarrow \gamma_r$
13	16	10.2	12.2	10.2	1/2/ π //1w/1w	y	L1,R2,L3	$\alpha \rightarrow \gamma_r$
14	68	18.6	9.52	10.3	1/2/ π //1s/0	y	L1,R2,L3	$\alpha \rightarrow \gamma$
15	49	15.7	11.4	11.0	1/2//0/1s,1w	n	L1,R2,L3	$\gamma \rightarrow \alpha$
16	100	23.0	13.3	11.3	2/2//0/1s,1w	n	L1,R2,L3	free
17	38	14.1	14.1	13.2	0/2/ π //1w/1w	y	R2,L3	$\alpha \rightarrow \gamma$
18	72	19.0	14.9	13.5	1/2/ π //1w/1w	y	R2,L3	$\alpha \rightarrow \gamma_r$
19	40	14.4	16.5	13.9	2/2//1w/0	y	L1,R2,L3	$\alpha \rightarrow \gamma$
20	56	17.1	14.7	14.7	0/2/ π //1w/1w	y	R2,L3	$\alpha \rightarrow \gamma$
21	9	7.75	78.9	71.4	0/2//1s/1s,1w	n	L1,R2,L3	$\alpha \rightarrow \gamma_r$

^a This structure was optimized starting from the assigned structure for conformer C in the K^+ species (conformer #52) and replacing the K^+ with a Na^+ ion. ^b This structure is the same as 11a from the Li^+ adduct conformation search. ^c s = strong, w = weak. The nomenclature “/ π ” denotes a $\text{Li}^+\cdots\pi$ interactions. ^d The three linkages are labeled L1, L2, and L3 with respect to the guaiacol (g) end of the tetramer and the three rings are labeled R1, R2, and R3. ^e The C6 hydrogen bond at the hinge position is denoted $\alpha \rightarrow \gamma$, or $\gamma \rightarrow \alpha$ to represent the relative orientation of the α and γ OH groups. The subscript “r” is an abbreviation for “rotamer” and applies to the L2 γ group. The γ C5 H-bond is between the L2 γ OH and aryl ether group of R3. ^f This structure is the same as 11a from the Li^+ adduct conformation search.

TABLE S.3: Calculated Energies of G-Type β -O-4 Tetramer K^+ Adducts Obtained from an MCMM Search

DFT Order	Force Field Order	MMFFs Energy (kJ·mol ⁻¹)	DFT Single Point Energy (kJ·mol ⁻¹)	Zero-Point Corrected (kJ·mol ⁻¹)	Number of $K^+\cdots OH/K^+\cdots OR/\pi//K^+\cdots OH\cdots OH/K^+\cdots OH\cdots OR$ Interactions ^b	$K^+\cdots OH\cdots OH\cdots OH(R)$ Present y/n	Pocket ^c	Hinge Type ^d
1	28	15.0	0.461	0	1/2/ π //1s/0	y	L1,R2,L3	$\alpha\rightarrow\gamma$
2	1	0	2.54	2.37	1/2/ π //0/1s,1w	n	L1,R2,L3	$\alpha\rightarrow\gamma$
3	49	16.9	4.81	4.85	1/2/ π //1s/0	y	L1,R2,L3	free
4	15	12.9	5.41	4.87	1/2/ π //1s/0	y	L1,R2,L3	$\alpha\rightarrow\gamma_r$
5	86	20.5	7.59	5.08	1/2/ π //0/1s	n	L1,R2,L3	free
6	52	17.3	0	5.32	0/2/ π //1w/1s,1w	y	L1,L3,R4	free
7	68	19.6	1.41	6.42	0/2/ π //1s/2s	n	L1,L3,R4	$\alpha\rightarrow\gamma_r$
8	50	17.1	10.2	7.37	0/3//1s/1s	n	L1,R2,L3,R4	free
9	11a ^a	---	7.99	9.46	0/2//1s/1s,1w	n	L1,R2,L3	$\alpha\rightarrow\gamma$
10	33	15.2	10.8	9.71	1/2/ π //1w/1s	n	L1,L3,R4	free
11	71	19.7	8.35	12.2	0/2//1s/1s,1w	n	L1,L3,R4	free
12	30	15.1	15.9	12.7	0/4/ π //1s/0	y	L1,L3,R4	γ C5
13	41	16.1	11.7	13.8	0/2//1s/1s,1w	n	L1,R2,L3	$\gamma\rightarrow\alpha$
14	75	20.0	13.4	14.0	0/2/ π //2s/0	n	L1,R2,L3	free
15	19	13.5	14.3	14.1	0/2//1s/1s,1w	n	L1,R2,L3	γ C5
16	69	19.6	14.9	14.6	0/2/ π //2s/1s	y	R1,L3,R4	free
17	5	9.11	19.7	15.6	1/3/ π //1s/0	y	L1,R2,L3,R4	γ C5
18	97	21.3	18.4	17.4	0/3/ π //1s/1s	y	L1,R2,L3,R4	$\alpha\rightarrow\gamma_r$
19	35	15.2	21.3	17.6	1/3/ π //1s/0	n	L1,R2,L3,R4	γ C5
20	38	15.6	21.3	17.6	1/3/ π //1s/0	y	L1,R2,L3,R4	γ C5
21	2	0.276	16.1	17.6	0/4/ π //1s/0	y	R2,L3,R4	$\alpha\rightarrow\gamma$

^a This structure is the same as 11a in the Li⁺ species but replaces the Li⁺ with a K⁺. ^b s = strong, w = weak. The nomenclature “/ π ” denotes a Li⁺ $\cdots\pi$ interactions.

^c The three linkages are labeled L1, L2, and L3 with respect to the guaiacol (g) end of the tetramer and the three rings are labeled R1, R2, and R3. ^d The C₆ hydrogen bond at the hinge position is denoted $\alpha\rightarrow\gamma$, or $\gamma\rightarrow\alpha$ to represent the relative orientation of the α and γ OH groups. The subscript “r” is an abbreviation for “rotamer” and applies to the L2 γ group. The γ C₅ H-bond is between the L2 γ OH and aryl ether group of R3.

Fig. S.2. Scatterplot showing relationship between relative force field energy and relative DFT (M05-2X/6-31G*) single point energy in the case of the Li^+ species. The correlation is weak, at best, emphasizing the need to perform many DFT geometry optimizations calculations to fully explore the potential energy surfaces of the tetramers.

Fig. S.3. Structures of low-energy Li^+ cationized β -O-4 tetramers: (a) Two views of the global minimum structure with circled $\text{Li}^+\cdots\text{OH}\cdots\text{OH(R)}$ interactions, (b) Conformer 11 from the MMFFs conformational search, and (c) the manually altered conformer (11a), in which the L2 hinge OH groups were rotated into an $\alpha\rightarrow\gamma$ configuration. Critical H-bond distances and angles are also indicated. The nomenclature describing each interaction as well as the relative zero-point corrected DFT energy is given below each structure. These correspond to the Table S.1 entries.

Fig. S.4. Calculated global minimum structures at the M05-2X/6-31G* level of theory for the (a) Li^+ , (b) Na^+ , and (c) K^+ adducts of G-type β -O-4 lignin tetramers. The left structure in each panel is displayed for optimal clarity of the metal cation binding pocket, while the right structure is rotated to display the linkage group (L2). The H-bonding environment and pocket location nomenclature is given for each structure and the “hinge” type is also pointed out (i.e., $\alpha \rightarrow \gamma$ vs. $\gamma \text{ C}_5$).

To explore the energetic impact of the various structural motifs, the optimized geometries of the Li^+ species (*cf.*, Lowest100DFT.xls) were sorted according to key structural characteristics (Table S.1). Figures S.5, S.6, S.7, S.8, and S.9 plot the relative single-point energies of the conformers of the Li^+ adducts against the number of $\text{Li}^+\cdots\text{O}$ interactions, hinge type, pocket location, presence of $\text{Li}^+\cdots\pi$ interactions, and presence of $\text{Li}^+\cdots\text{OH}\cdots\text{OH}\cdots\text{OR}$ interactions, respectively. The large spread in the energies of these conformers implies a complex balance between the energetic advantages and disadvantages of various H-bonding environments, pocket locations, sterics, etc., which mitigates a clear delineation of the conformers into structural families. The clearest pattern that emerges from these plots is that structures that are pentacoordinate with respect to $\text{Li}^+\cdots\text{O}$ interactions tend to be lowered in energy (Fig. S.5). Note that pentacoordinate conformers were extracted from the plot and separated sorted according to each of the other structural characteristics (*i.e.*, hinge type, binding pocket location, etc.) but no clear pattern emerged to define a secondary factor that influences the energetic ordering.

A notable difference between the Li^+ , Na^+ , and K^+ species (*cf.* Tables S.1-S.3 and Fig. S.8) is the increase in the number of low energy conformers with $\text{M}^+\cdots\pi$ interactions as the size of the cation increases (2 for Li^+ , 11 for Na^+ , and 16 for K^+). In the context of Lewis acids, this observation is intuitive because the K^+ ion, which has a larger ionic radius, is “softer” than the Li^+ ions and should bind more strongly to “softer” ligands, such as the aromatic rings. In fact, from examining Table S.3 it can be seen that the criterion of five $\text{M}^+\cdots\text{O}$ interactions is relaxed as the π interaction can occupy a coordination site. The Na^+ ion has a smaller ionic radius than the K^+ ion, making it a “harder” cation but not as hard as Li^+ , accounting for the intermediate behavior (Table S.2).

Fig. S.5. Dependence of relative conformer energy (single point energy at the M05-2X/6-31G* level of theory) on the number of Li⁺···O interactions. Although there is a large energetic spread, most of the low-energy conformers are pentacoordinate (blue) with respect to chelation by OH(R) groups. The color code of the horizontal bars is defined on the top of the plot.

Fig. S.6. Dependence of the relative conformer energy (single point energy at the M05-2X/6-31G* level of theory) on the type of “hinge” group (*i.e.*, direction and type of H-bond at the L2 linkage). The numbers and color code representing each type of hinge group are listed in the bottom right corner of the figure. This plot shows no clear correlation between the type of hinge group and the energetic ordering of the conformers.

Fig. S.7. Dependence of the relative conformer energy (single point energy at the M05-2X/6-31G* level of theory) on the location of the metal cation binding pocket (defined by the linkages L_n and rings R_m that donate O atoms to the $\text{Li}^+\cdots\text{O}$ bonds). The numbers and color code representing each type of binding pocket are listed in the bottom right corner of the figure. This plot shows no clear correlation between the binding pocket location and the energetic ordering of the conformers.

Fig. S.8. Dependence of the relative conformer energy (single point energy at the M05-2X/6-31G* level of theory) on presence of $\text{Li}^+ \cdots \pi$ interactions. Structures with no (blue) $\text{Li}^+ \cdots \pi$ interactions tend to be lower in energy than ones with (red) $\text{Li}^+ \cdots \pi$ interactions, with only two exceptions.

Fig. S.9. Dependence of the relative conformer energy (single point energy at the M05-2X/6-31G* level of theory) on presence of $\text{Li}^+\cdots\text{OH}\cdots\text{OH}\cdots\text{OR}$ interactions. Many more structures were found without these interactions (blue); however, no clear energetic preference exists.

In Fig. S.10, calculated harmonic level spectra [M05-2X/6-31+G*] are shown for each of the global minima structures from the conformational searches. Based on the inadequate comparison between these calculated spectra and the conformation-specific photofragment depletion spectra, it is unlikely that any of these structures were experimentally observed. For example, in the most dominant conformer of the Li^+ species, seven distinct bands were observed above 3450 cm^{-1} , which correspond to each of the seven OH oscillators. Therefore, the calculated α_3 transition in the global minimum structure (3322 cm^{-1}) is too far red-shifted to explain this conformer. Furthermore, the empirical assignment of the guaiacol OH stretch at 3591 cm^{-1} (discussed in Section III.C of the manuscript) requires three OH transitions that are red-shifted with respect to the guaiacol OH. Clearly, this is not the case upon examination of trace (a) of Fig. S.10, which contains only two OH stretches that are red-shifted relative to the guaiacol OH. Furthermore, none of the less intense isomers displayed band patterns that could easily account for the calculated global minimum structure (Fig. S.14).

Similar arguments apply when comparing the calculated global minima of the Na^+ and K^+ adducts to the experimental photofragment depletion spectra. In fact, both of these spectra show a red-shifted guaiacol OH stretch, which is engaged in an additional strong H-bond across the oligomer. Each of the experimental spectra obtained contains an OH stretch within a few wavenumbers of 3590 cm^{-1} , which show a strong empirical comparison to the guaiacol OH stretch that was previously observed in the neutral monomers⁷ and dimers,⁸ and in the metal cationized dimers.⁹ The fact that the global minima structures are not observed in the experimental infrared spectra suggests two likely possibilities: (1) these conformers are much weaker, and possibly broader, than the sharp and distinct transitions in the UV action spectra, or (2) the conformational searches are incomplete, which may be likely based on the poor correlation between the DFT and

force field energies (Fig. S.2). Rather than further speculating on this matter, which may require advanced theoretical methods to unravel, we focus on the structural information that is present in the experimental spectra at hand.

Fig. S.10. Calculated harmonic level spectra [M05-2X/6-31+G*] of global minima structures of the (a) Li^+ , (b) Na^+ , and (c) K^+ adducts. Each stick is labeled according to its corresponding OH stretching oscillator.

V. UVPD, CID, and DDC Mass Spectra of the Li⁺ Adduct

Figure S.11 shows expansions of the UV photofragment dissociation (UVPD) mass spectrum of the Li⁺ cationized β -O-4 tetramer. Similar to the manuscript (Figs. 2-4), the UVPD mass spectra are depicted in cases of low and high laser fluence, which were achieved by defocusing and focusing the UV laser in the center of the cold trap, respectively. As the fluence is increased, many small molecule loss channels gain intensity relative to the back-bone fragments (*i.e.*, A2 and B2) and several of these display multiplet patterns that are not characteristic of simple isotope distributions. For example, the -H₂O and -CH₂O losses from the B2 fragment contain peaks that are lighter by 1 and 2 m/z units and the B2 fragment appears to be most abundant after an additional loss of m/z = 2. Thus, the isotopic resolution suggests that H or H₂ is often lost in addition to the main fragment channels.

Fig. S.11. Expanded resonant UV ($35,111\text{ cm}^{-1}$) photofragment mass spectrum of the Li^+ adduct showing isotopic resolution. Traces (a) and (b) show the A2 and B2 fragment channels ($m/z = 320-410$), while traces (c) and (d) show small molecule losses from the parent ion ($m/z = 600-700$). The mass spectra are shown in cases of low laser fluence [(a) and (c)] as well as high laser fluence [(b) and (d)].

To evaluate the mechanism by which photofragments are produced, we compared the resonant UVPD mass spectra to ion trap CID mass spectra taken on our home-built 3D ion trap mass spectrometer.¹⁰ This comparison is shown in Fig. S.12, which displays a clear similarity between the fragmentation patterns generated by both dissociation techniques. The most notable difference between the UVPD and CID mass spectra is the relative abundance of the single H₂O and CH₂O+H₂O losses, which are more abundant by CID than by UVPD. Such a difference can be rationalized because ion trap CID slowly increases the internal energy of the ions after numerous collisions with buffer gas molecules on a millisecond timescale,¹¹ while the resonant UV excitation occurs on the order of 8 ns.^{12,13} The slow, adiabatic heating process during CID allows the ions to follow the minimum energy path to dissociation, while the 8 ns UV excitation raises the internal energy faster than molecular rearrangements can occur, potentially allowing many pathways provided that the photon energy is greater than the dissociation barriers. Because the main fragmentation channels are similar in the CID and UVPD mass spectra, the UVPD dissociation process likely occurs after internal conversion to S₀. This process differs from the excited state mechanism proposed for the UVPD of peptides containing aromatic side chains (Phe, and Tyr),^{12,13} which show a side chain loss that is not observed in CID mass spectra. Unfortunately, the similarity between the CID and UVPD suggests that UV photoexcitation cannot be used to selectively cleave particular bonds by individual resonant excitation of each of the rings in the β -O-4 tetramer. However, we have thus far examined one linkage and monomer type and selective excited state fragmentation processes may become more relevant in systems with mixed linkages and monomers.

Fig. S.12. Comparison of the (a) CID mass spectrum of the Li^+ adduct taken on a home-built 3D ion trap mass spectrometer to the (b) UVPD mass spectrum taken on the photofragmentation spectroscopy instrument. The backbone fragments are labeled in red and are consistent with Fig. 2-4 in the manuscript. Although the loss of H_2O and $\text{CH}_2\text{O}+\text{H}_2\text{O}$ is much more abundant in the CID mass spectrum, the backbone fragments and additional small molecule loss channels in the CID mass spectrum (expanded $\times 3$) show a similar pattern to the UVPD mass spectrum. The peak labeled with a * is a Na^+ adduct contaminant, which bled through the mass isolation of the 3D ion trap.

VI. Time-Dependent Density Functional Theory

In Table S.4, the first four computed electronic excitations are listed along with their oscillator strengths for each of the assigned structures of the Li^+ , Na^+ , and K^+ adducts. Strong electronic coupling between the aromatic rings is likely, as evidenced by the delocalized nature of the frontier molecular orbitals. An example of these orbitals are shown in the case of conformer A of the Li^+ species (Fig. S.13). We suspect that the broad nature of the electronic spectra is a manifestation of these strong couplings.

TABLE S.4: Vertical Excitation Energies and Oscillator Strengths for Assigned Conformers Calculated by TDDFT at the M052X/6-31+G* Level of Theory.

		Wavenumber (cm^{-1}) ^a	Oscillator Strength
Li^+ Conformer A	$\text{S}_1 \leftarrow \text{S}_0$	34646	0.0514
	$\text{S}_2 \leftarrow \text{S}_0$	35009	0.0985
	$\text{S}_3 \leftarrow \text{S}_0$	35420	0.0402
	$\text{S}_4 \leftarrow \text{S}_0$	36533	0.0756
Na^+ Conformer A	$\text{S}_1 \leftarrow \text{S}_0$	34917	0.0346
	$\text{S}_2 \leftarrow \text{S}_0$	35038	0.0954
	$\text{S}_3 \leftarrow \text{S}_0$	35658	0.0429
	$\text{S}_4 \leftarrow \text{S}_0$	36489	0.0798
Na^+ Conformer C	$\text{S}_1 \leftarrow \text{S}_0$	34195	0.0488
	$\text{S}_2 \leftarrow \text{S}_0$	34932	0.0536
	$\text{S}_3 \leftarrow \text{S}_0$	35446	0.0098
	$\text{S}_4 \leftarrow \text{S}_0$	35903	0.0501
K^+ Conformer C	$\text{S}_1 \leftarrow \text{S}_0$	34152	0.046
	$\text{S}_2 \leftarrow \text{S}_0$	34913	0.0562
	$\text{S}_3 \leftarrow \text{S}_0$	35476	0.0094
	$\text{S}_4 \leftarrow \text{S}_0$	36008	0.0591

^a All vertical excitation wavenumbers were scaled by 0.8384 to assure agreement between the calculated and measured $\text{S}_1 \leftarrow \text{S}_0$ transition in conformer A of the neutral β -O-4 dimer.⁸

Fig. S.13. Frontier molecular orbitals calculated for conformer A of the Li^+ adduct. Each of the unoccupied orbitals is delocalized over multiple rings, especially between two center rings that stack face-to-face.

VII. Extended UV Action Spectrum

An extended UV action spectrum of the Li^+ adduct is given in Fig. S.14. As discussed in the manuscript, the sharp features are close in wavenumber to the origin region of the dimer cations,⁹ which were previously assigned to excitation of the guaiacol ring.^{7,8} The transitions near $35,700\text{ cm}^{-1}$ are likely attributed to one or more of the other aromatic rings and are proximal to the origin bands in 1,2-dimethoxybenzene,⁷ a model compound for the last ring in the oligomer (opposite from the guaiacol end). It is likely that the close energetic proximity of the four chromaphores leads to strong vibronic coupling that broadens the UV spectrum. Unraveling the complexities of the electronic structures of these tetramers warrants further study. However, in the manuscript we focus on the sharp features in the UV action spectrum, which allowed us to obtain conformation-specific infrared spectra.

Fig. S.14. Extended UV action spectrum of the Li^+ species (34200-35800 cm^{-1}). The spectrum has been power normalized to account for the difference in laser power between the two dye ranges (Rhodamine 6G above 35450 cm^{-1} and 50:50 Rhodamine 6G:Rhodamine B below 35450 cm^{-1}).

VIII. Conformation-Specific Infrared Spectra of Minor Conformers in the Li^+ Species

The conformation-specific infrared spectrum of several minor isomers is given in Fig. S.15. The infrared spectrum was also taken by the photofragment ion gain (IRFIG) method, in which the UV laser was tuned off resonance to the red of the sharp transitions ($35,000\text{ cm}^{-1}$). This spectrum shows contributions from all of the isomers. However, the weak relative abundance of the distinct transitions associated with conformer A (*e.g.*, 3617 cm^{-1}) suggests that either the summation of the infrared spectra of the remaining isomers dwarfs this transition in the IRFIG spectrum or that the UV probe wavenumber was too far to the red to observe substantial photofragment gain from the IR resonant absorption of conformer A. Although it is apparent that A, E, G, and D all arise from different conformers, the low signal to noise attributed to the high photofragment background (*cf.*, broad background in Fig. 5 of manuscript) complicates the analysis, especially for conformers G and D. In Fig. S.16, the spectrum of conformer F of the K^+ species is also shown. This conformer appears to have some similarities with conformer C in the K^+ adduct; however, the low signal to noise makes it difficult to distinguish each of the seven OH transitions.

Fig. S.15. Conformation-specific infrared spectra of the Li^+ species: (a) A, (b) E, (c) G, (d) D, where the capital letters refer to the transitions labeled in the UV action spectrum (manuscript Fig. 5). The infrared spectrum taken by photofragment ion gain (IRFIG) is shown in trace (e), as well as the calculated harmonic level spectrum that is tentatively assigned to conformer A.

Fig. S.16. IR photofragment depletion spectrum of conformer F of the K^+ species.

IX. Sensitivity of the “Hinge” $\alpha \rightarrow \gamma$ OH Stretching Transition

To illustrate the sensitivity of the “hinge” OH group (α_2), the calculated harmonic level spectra of both the tentatively assigned structure for conformer A (a) and the calculated global minimum structure (b) are presented in Fig. S.17. Although the α_2 OH groups occupy similar chemical environments (both $\alpha \rightarrow \gamma$ H-bonds), the OH $\cdots$ O distance is greater (1.94 vs. 1.87 Å) in the global minimum structure and the OH $\cdots$ O angle decreases (136.0° vs. 140.2°). These geometric changes are consistent with a weakened H-bond, which leads to a blue-shifted α_2 OH stretching fundamental in the calculated global minimum structure (3575 vs. 3557 cm⁻¹). Such a blue shift implies that structural differences associated with charge accommodation of the metal cation can influence the torque on the remote “hinge” group, leading to observable shifts in the α_2 vibrational frequency. Given this sensitivity, it is likely that the α_2 OH stretching vibration is also affected by the level of electronic structure theory that describes the charge center, which may flex the “hinge” group depending on the strength of the metal cation chelation.

Fig. S.17. Calculated harmonic-level spectra of (a) the tentatively assigned conformer A and (b) the calculated global minimum conformer for the Li^+ species. The peak highlighted in blue is the α_2 OH stretch at the “hinge” position, which is shown to shift by 17 cm^{-1} between the two conformers, despite the similar chemical environment. Structures of both conformers are also illustrated, highlighting the OH...O distance and angle (θ) for both hinge positions.

X. Extended Conformation-Specific Infrared Spectrum of Conformer B

An extended photofragment depletion infrared spectrum of conformer B is provided in Fig. S.18. The spectrum does not show any distinct OH stretching transitions between 2800 cm^{-1} and 3540 cm^{-1} , suggesting that this conformer does not contain any strong $\text{K}^+\cdots\text{OH}\cdots\text{O}$ interactions. The weak and broad feature near 3000 cm^{-1} occurs in the expected location of CH stretching. The spectrum between 2800 and 3350 cm^{-1} is a single scan and between 3350 and 3700 cm^{-1} is the average of six scans.

Fig. S.18. Extended photofragment depletion IR spectrum of conformer B of the K^+ adduct ($2800\text{--}3700\text{ cm}^{-1}$). The spectrum is an average of six scans above 3350 cm^{-1} and consists of a single scan below 3350 cm^{-1} .

XI. Background Subtraction of Photofragment Depletion Spectra

In cases in which the IR-induced photofragment gain of additional conformers overlapped with the photofragment depletion signal of the probed conformer, it was necessary to subtract this photofragment gain background to reveal the conformation-specific infrared spectrum. An example of this background is provided in Fig. S.19, where the red trace corresponds to the IR spectrum when the UV laser was fixed on resonance with conformer C ($34,834\text{ cm}^{-1}$) of the K^+ species. To eliminate this background from the photofragment depletion spectrum the UV laser was tuned a few wavenumbers to the red off-resonance ($34,830\text{ cm}^{-1}$) and the photofragment gain spectrum was obtained (black trace). The spectra were subtracted to give the photofragment depletion spectrum reported in the manuscript Fig. 9. The same background subtraction procedure was followed for conformers B and C of both the Na^+ and K^+ species in addition to the spectra shown in Fig. S.15 and S.16.

Fig. S.19. Example of raw IR spectra prior to background subtraction. The red trace is the infrared spectrum taken with the UV laser on resonance with conformer C in the K^+ species ($34,834\text{ cm}^{-1}$). The black trace is an IR-induced photofragment gain background spectrum taken with the UV laser a few wavenumbers off resonance ($34,830\text{ cm}^{-1}$).

XII. Extended K⁺ Conformer Energies

A series of extended conformers were optimized at the M05-2X/6-31+G* level of theory to assess the possibility that conformer B contains discrete neutral and cationized dimer linkages. In naming these structures, we adopt notation based on Fig. 1 (see manuscript), where the type of linkages Ion (I) vs. Neutral (N) are first specified, followed by the conformers that correspond to each linkage (A, B, or C for I and A or B for N). For example, the lowest energy of these structures [Ion(B)-Neutral(B)-Neutral(B) denoted I_BN_BN_B] is shown in Fig. S.20 and its calculated harmonic spectrum is given in Fig S.21(c). The relative energies of these conformers are given in Table S.5, which are all far greater than the calculated global minimum energy from the MCMM conformational search. Although the energies in Table S.5 are not zero-point corrected, we performed vibrational frequency calculations on a handful of these structures and observed harmonic-level spectra that were all similar to trace (c) in Fig. S.20.

Fig. S.20. Lowest energy extended structure of the K^+ adduct containing a dimer ion (I) and two neutral (N) linkages: $I_B N_B N_B$ (see text for nomenclature).

Fig. S.21. Comparison of the IR-UV double resonance photofragment depletion spectra of Na^+ (a) and K^+ (b) adducts of the G-type β -O-4 tetralignol complex with the UV laser fixed on the B transition (manuscript Table 1). The spectra of the tetramer ions are also compared to the calculated harmonic level spectrum of the $\text{I}_\text{B}\text{N}_\text{B}\text{N}_\text{B}$ conformer of the K^+ species (c) and to ion gain spectra of the sodium cationized⁹ (d) and neutral⁷ (e) dimers.

TABLE S.5: Relative Energies of Extended Conformers of the K⁺ Species

	<i>l</i>	<i>m</i>	<i>n</i>	Relative Energy (kJ/mol)
I _l N _m N _n	A	A	A	58.9
	A	A	B	59.0
	A	B	A	63.4
	A	B	B	61.1
	B	A	A	57.2
	B	A	B	53.9
	B	B	A	60.0
	B	B	B	51.5
	C	A	A	55.8
	C	A	B	55.9
	C	B	A	61.5
	C	B	B	55.9
N _l N _m I _n	A	A	A	81.9
	A	A	B	80.5
	A	B	A	88.6
	A	B	B	89.4
	B	A	A	89.8
	B	A	B	88.6
	B	B	A	93.3
	B	B	B	93.8
	A	A	C	80.4
	A	B	C	89.5
	B	A	C	88.6
	B	B	C	93.7
N _l I _m N _n	A	A	A	*
	A	A	B	74.4
	A	B	A	69.7
	A	B	B	72.7
	B	A	A	77.7
	B	A	B	80.7
	B	B	A	*
	B	B	B	81.9
	A	C	A	68.7
	A	C	B	73.7
	B	C	A	77.5
	B	C	B	*

* indicates a geometry convergence failure.

XIII. Conformer B Theoretical Comparison

A comparison of the conformation-specific infrared spectrum of conformer B to the calculated harmonic level spectrum of the lowest-energy conformer (15.2 kJ·mol⁻¹ above the global minimum) from the MCMM search that contains no strong M⁺...OH...O interactions is given in Fig. S.22. Although this conformer lacks the strong M⁺...OH...O interactions that give rise to the highly red-shifted bands observed in the other conformers, the furthest red-shifted transition is the guaiacol OH stretch. The experimental spectrum shows one strong band at 3550 cm⁻¹, which is red-shifted from the guaiacol OH stretching transition. Thus, we have ruled out the feasibility of this structure based on the poor comparison between its harmonic level spectrum and the experimental data in addition to its high relative energy.

Fig. S.22. A comparison between the IR-UV double resonance photofragment depletion spectrum of conformer B (a) and the calculated harmonic-level spectrum (M05-2X/6-31+G*) of the lowest-energy conformer containing no strong $\text{M}^+\cdots\text{OH}\cdots\text{O}$ interactions (b). Two views of the 3D structure of this conformer are also given in trace (b) with labeled OH oscillators.

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