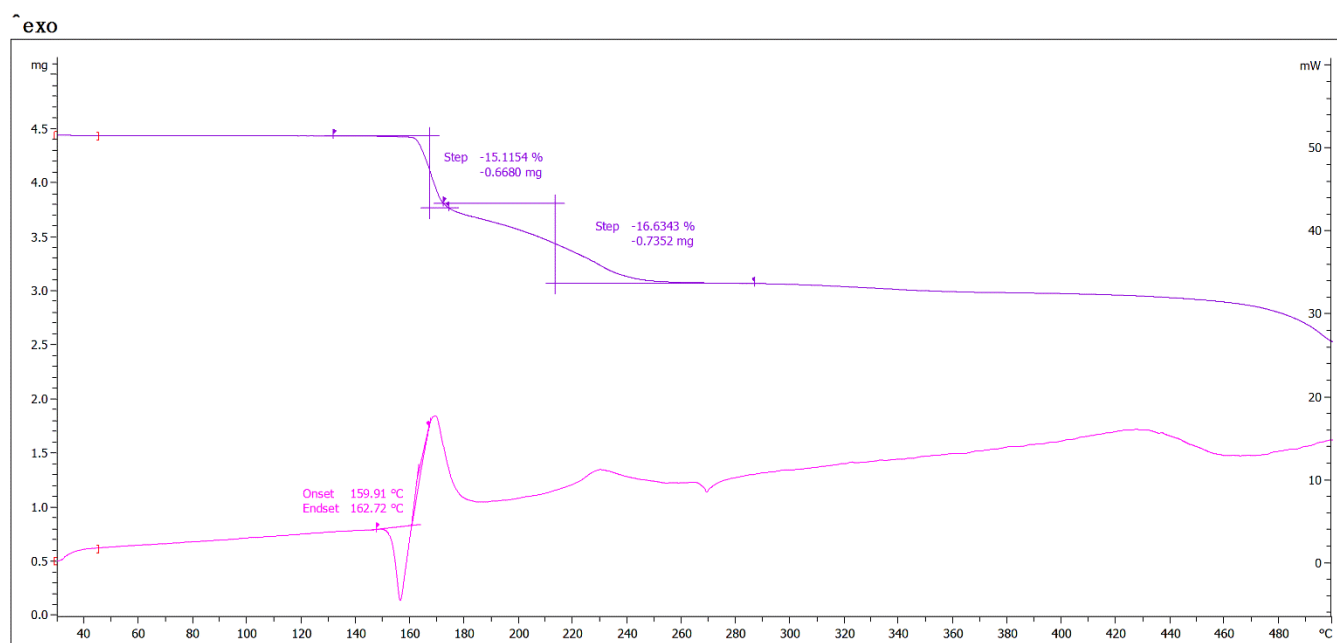


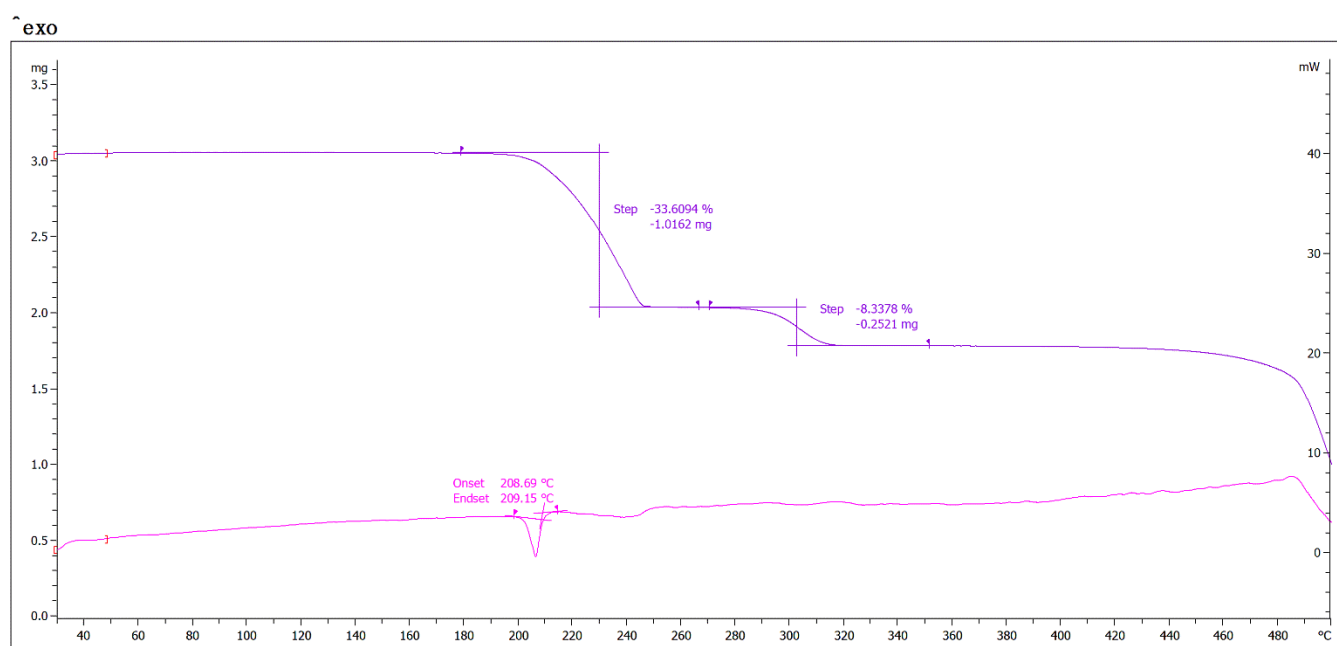
## Supplementary Information

### The Impact of Structural Changes in Heteroleptic Bismuth Phosphinates on their Antibacterial Activity in Bi-nanocellulose Composites.

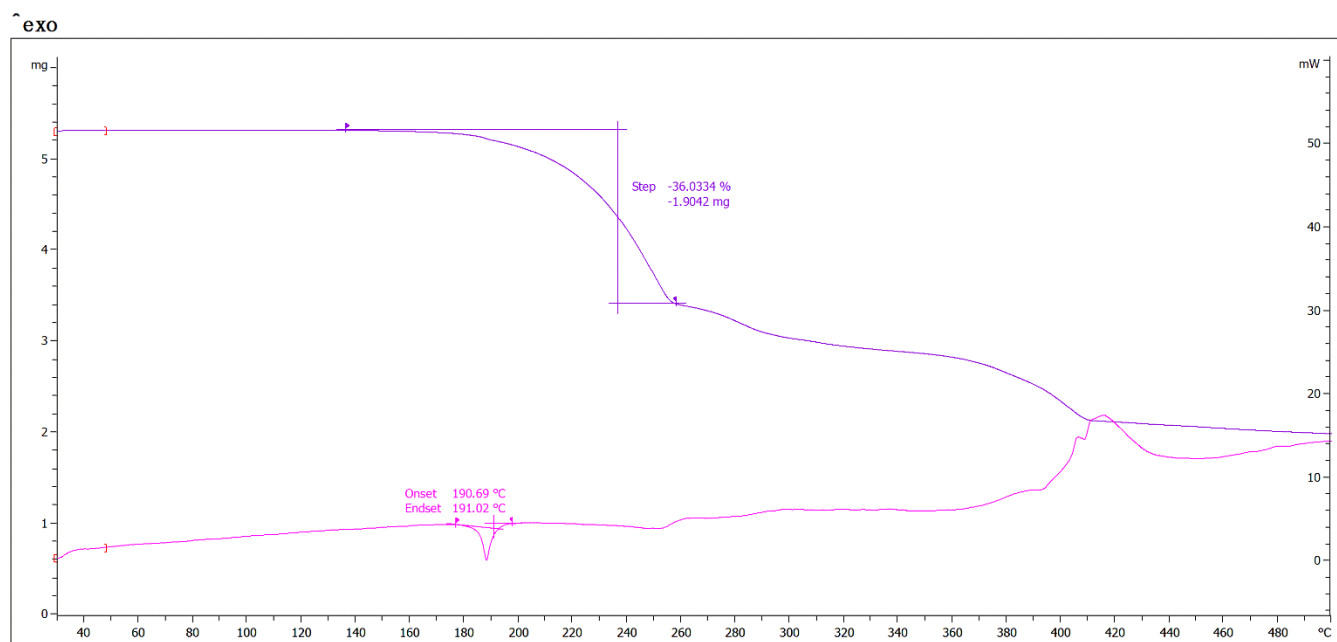
Megan E. Herdman,<sup>a</sup> Melissa V. Werrett,<sup>a</sup> Rebekah N. Duffin,<sup>a</sup> Liam Stephens,<sup>a</sup> Rajini Brammananth,<sup>b</sup>  
Ross L Coppel,<sup>b</sup> Warren Batchelor<sup>c</sup> and Philip C. Andrews<sup>a</sup>



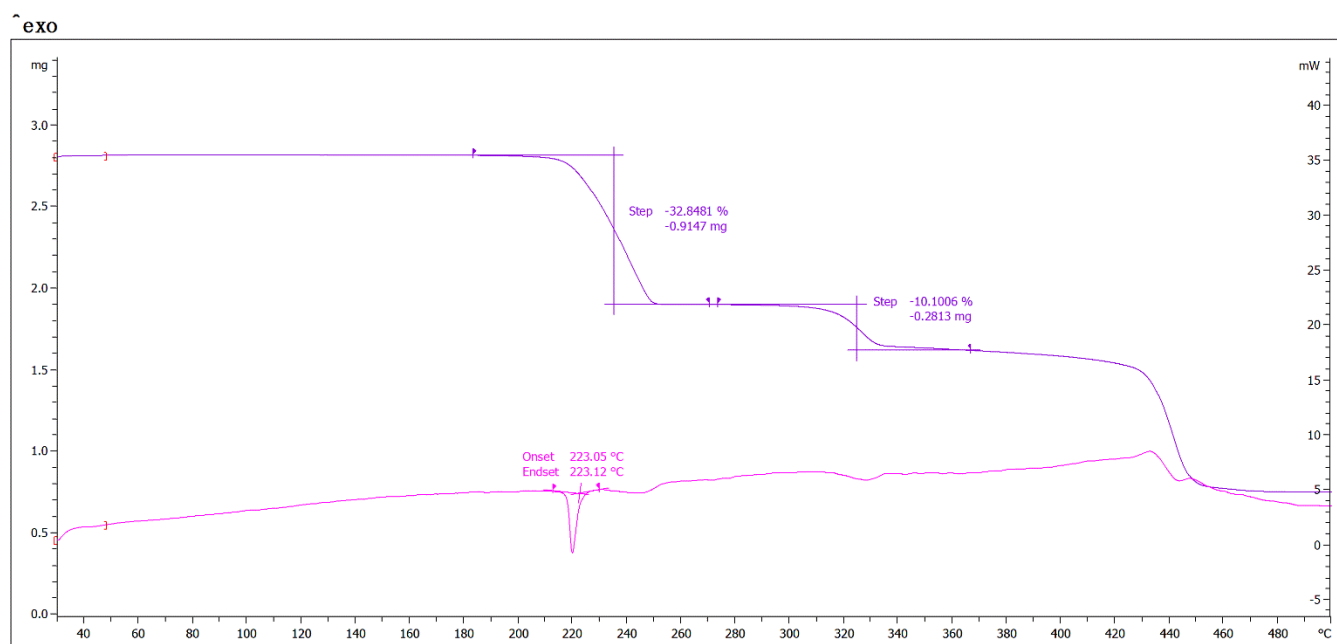
Lab: METTLER STAR® SW 10.00  
 Figure S1 – TGA (purple) and DSC (pink) trace for diphenyl *mono*-phenylphosphinato bismuth complex 1.



Lab: METTLER STAR® SW 10.00  
 Figure S2 – TGA (purple) and DSC (pink) trace for diphenyl *mono*-diphenylphosphinato bismuth complex 2.



Lab: METTLER STAR® SW 10.00  
 Figure S3 – TGA (purple) and DSC (pink) trace for diphenyl *mono*-dimethylphosphinato bismuth complex **3**.



Lab: METTLER STAR® SW 10.00  
 Figure S4 – TGA (purple) and DSC (pink) trace for diphenyl *mono*-(*bis*-4-methoxyphenyl)phosphinato bismuth complex **4**.

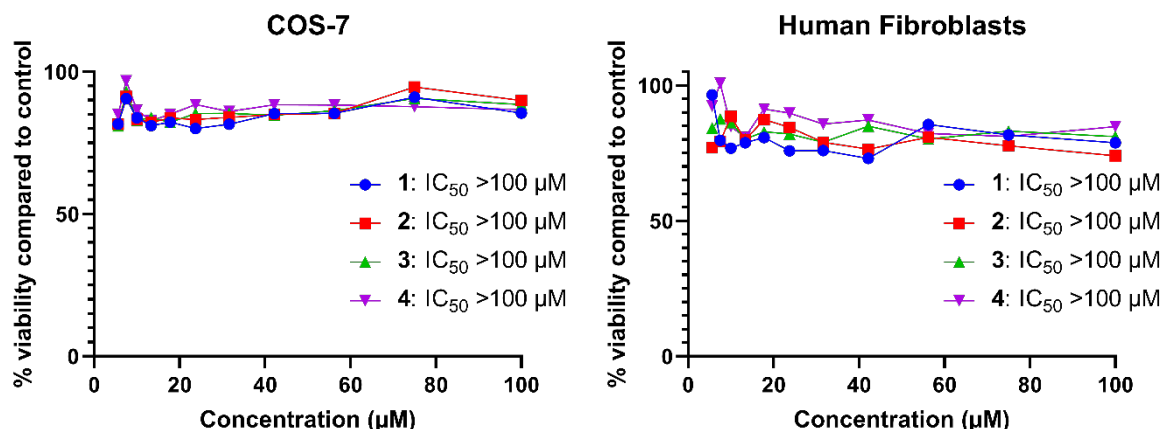


Figure S5 – Mammalian cell viability of COS-7 and human fibroblasts following 24 hour incubation to determine  $IC_{50}$  of phosphinic acids solubilised in DMSO: **1a** – phenylphosphinic acid, **2a** – diphenylphosphinic acid, **3a** – dimethylphosphinic acid and **4a** – *bis*-(4-methoxyphenyl)phosphinic acid.

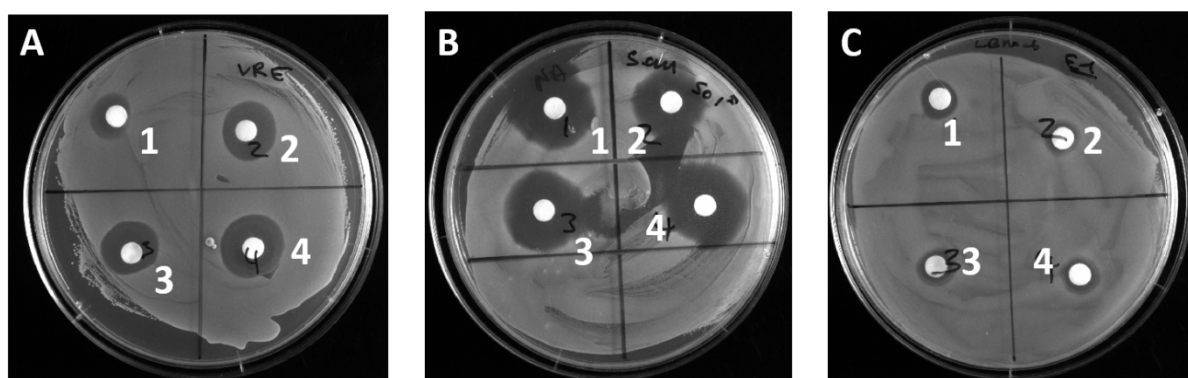


Figure S6 – Zones of inhibition following disc diffusion assay against VRE (A), *S. aureus* (B) and *E. coli* (C) for complexes **1-4** solubilised in DMSO at the following concentrations: [**1**] = 1.69 mM, [**2**] = 0.86 mM, [**3**] = 1.10 mM and [**4**] = 0.94 mM.

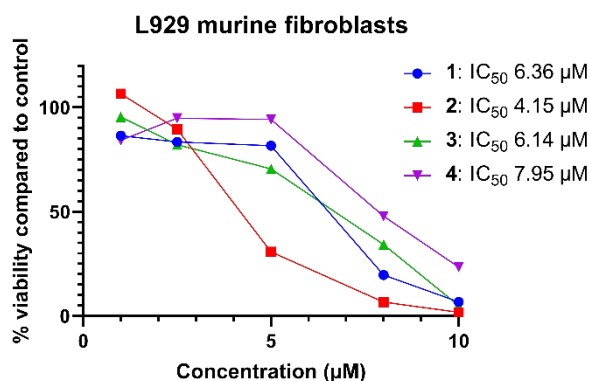


Figure S7 – Cell viability of L929 murine fibroblast using the MTS assay following 24 hour incubation to determine  $IC_{50}$  of complexes **1 – 4** solubilised in DMSO. A control of cells without compound addition was treated as 100 % viable and the maximum DMSO concentration (1 %) was also included as a control where the average viability was 90 %.

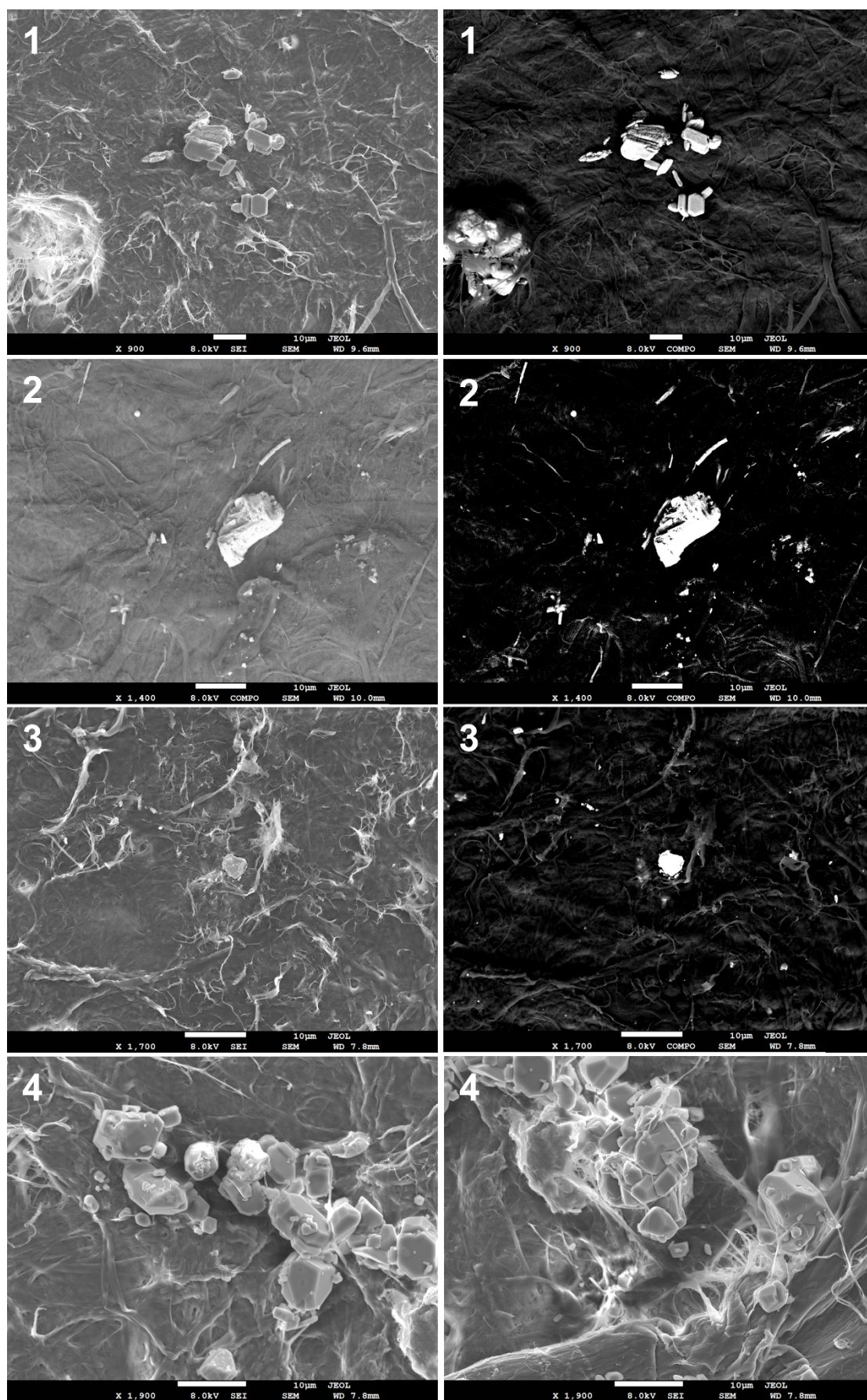


Figure S8 - SEM and backscatter electron images showing the morphology of the *mono*-phosphinato bismuth complexes **1-4**. Scale bars are 10 µm.

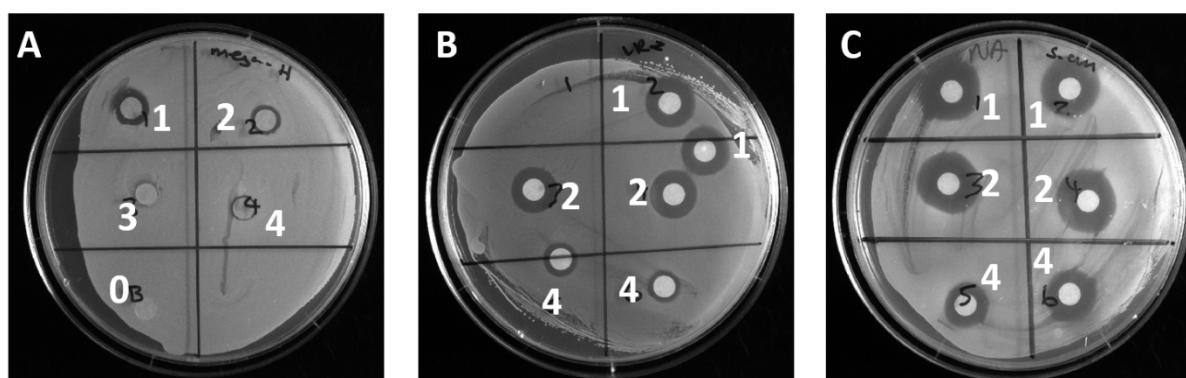


Figure S9 – MRSA (A), VRE (B) and *S. aureus* (C) zone of inhibition analysis for low-loading Bi-composites containing: **1** at 0.30 wt% loading, **2** at 0.31 wt% loading, **3** at 0.16 wt% loading and **4** at 0.20 wt% loading.

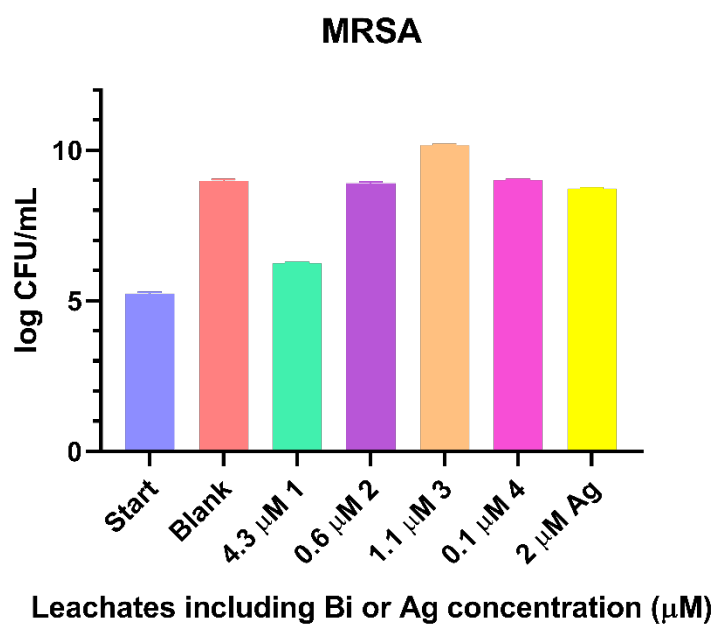


Figure S10 – Colony forming units following 24 hour incubation with MRSA broth and composite leachates (**1 – 4** and **Ag**). Concentration of Bi or Ag in the total solution is included in μM, as determined by the metal content in the leachate from ICP-MS.

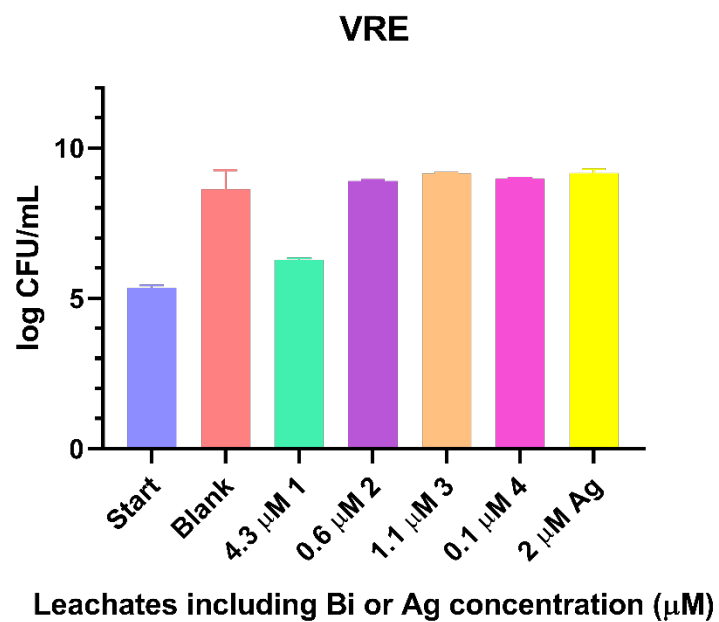


Figure S11 – Colony forming units following 24 hour incubation with VRE broth and composite leachates (**1 – 4** and **Ag**). Concentration of Bi or Ag in the total solution is included in  $\mu\text{M}$ , as determined by the metal content in the leachate from ICP-MS.

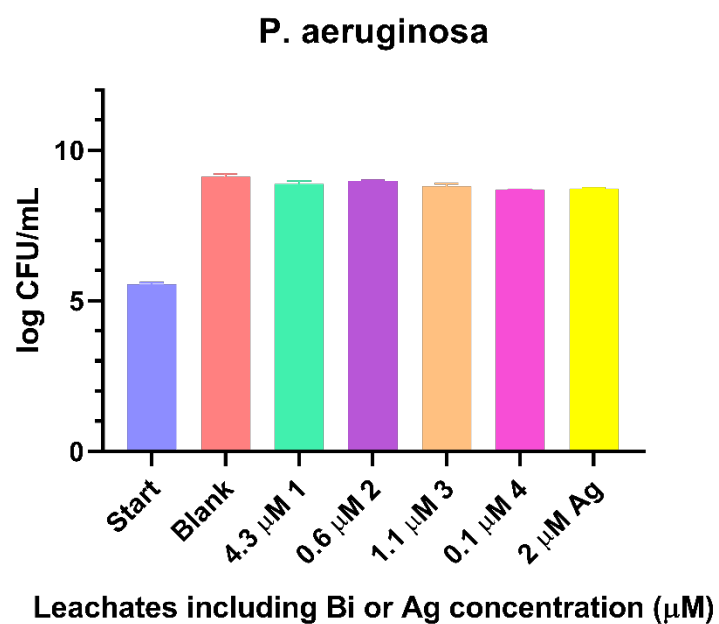


Figure S12 – Colony forming units following 24 hour incubation with *P. aeruginosa* broth and composite leachates (**1 – 4** and **Ag**). Concentration of Bi or Ag in the total solution is included in  $\mu\text{M}$ , as determined by the metal content in the leachate from ICP-MS.

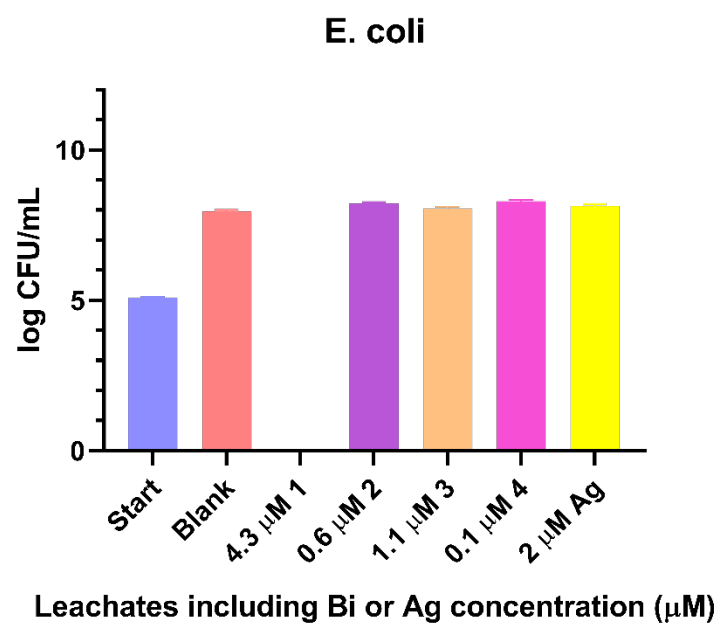


Figure S13 – Colony forming units following 24 hour incubation with *E. coli* broth and composite leachates (**1 – 4** and **Ag**). Concentration of Bi or Ag in the total solution is included in  $\mu\text{M}$ , as determined by the metal content in the leachate from ICP-MS.

Table S1 – Summary of crystal data for complexes **1-4**.

| Complex                            | [BiPh <sub>2</sub> (OP(=O)PhH)] <b>1</b>           | [BiPh <sub>2</sub> (OP(=O)Ph <sub>2</sub> )] <b>2</b> | [BiPh <sub>2</sub> (OP(=O)Me <sub>2</sub> )] <b>3</b> | [BiPh <sub>2</sub> (OP(=O)(PhOMe) <sub>2</sub> )] <b>4</b> |
|------------------------------------|----------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|------------------------------------------------------------|
| Formula                            | C <sub>18</sub> H <sub>16</sub> BiO <sub>2</sub> P | C <sub>24</sub> H <sub>20</sub> BiO <sub>2</sub> P    | C <sub>14</sub> H <sub>16</sub> BiO <sub>2</sub> P    | C <sub>26</sub> H <sub>24</sub> BiO <sub>4</sub> P         |
| Formula weight                     | 504.26                                             | 580.35                                                | 456.22                                                | 640.40                                                     |
| Crystal system                     | Monoclinic                                         | Orthorombic                                           | Orthorombic                                           | Monoclinic                                                 |
| Space group                        | C2/c                                               | P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>         | P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>         | P2 <sub>1</sub> / <i>n</i>                                 |
| <i>a</i> (Å)                       | 18.5068(11)                                        | 9.9875(5)                                             | 9.0005(2)                                             | 12.0180(3)                                                 |
| <i>b</i> (Å)                       | 8.9144(6)                                          | 11.0201(4)                                            | 16.2512(3)                                            | 10.7673(3)                                                 |
| <i>c</i> (Å)                       | 21.9738(18)                                        | 19.3941(7)                                            | 10.0290(2)                                            | 17.6146(4)                                                 |
| $\alpha$ (°)                       | 90                                                 | 90                                                    | 90                                                    | 90                                                         |
| $\beta$ (°)                        | 112.186(4)                                         | 90                                                    | 90                                                    | 94.874(2)                                                  |
| $\gamma$ (°)                       | 90                                                 | 90                                                    | 90                                                    | 90                                                         |
| Volume (Å <sup>3</sup> )           | 3356.8(4)                                          | 2134.58(15)                                           | 1466.93(5)                                            | 2271.11(10)                                                |
| <i>Z</i>                           | 8                                                  | 4                                                     | 4                                                     | 4                                                          |
| Density (g cm <sup>-3</sup> )      | 1.996                                              | 1.806                                                 | 2.066                                                 | 1.873                                                      |
| $\mu$ (mm <sup>-1</sup> )          | 10.604                                             | 17.045                                                | 24.557                                                | 16.159                                                     |
| <i>F</i> <sub>000</sub>            | 1904                                               | 1112                                                  | 856                                                   | 1240                                                       |
| <i>T</i> (K)                       | 123(1)                                             | 123.01(12)                                            | 123.00(13)                                            | 123.00(10)                                                 |
| 2 $\theta$ <sub>max</sub> (°)      | 55.0                                               | 133.9                                                 | 133.7                                                 | 134.1                                                      |
| Reflections collected              | 14755                                              | 7878                                                  | 15386                                                 | 15407                                                      |
| Unique reflections                 | 3858 ( <i>R</i> <sub>int</sub> = 0.0530)           | 3565 ( <i>R</i> <sub>int</sub> = 0.0357)              | 2595 ( <i>R</i> <sub>int</sub> = 0.0374)              | 4027 ( <i>R</i> <sub>int</sub> = 0.0389)                   |
| Final GooF                         | 1.003                                              | 1.033                                                 | 1.044                                                 | 1.071                                                      |
| <i>R</i> <sub>1</sub>              | 0.0280                                             | 0.0291                                                | 0.0192                                                | 0.0371                                                     |
| w <i>R</i> <sub>2</sub> (all data) | 0.0556                                             | 0.0724                                                | 0.0454                                                | 0.0774                                                     |
| Flack parameter                    |                                                    | -0.043                                                | -0.034(8)                                             |                                                            |