The water-soluble $\text{Re}_6$-clusters with aromatic phosphine ligands – from synthesis to potential biomedical applications

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Figure 2S. ¹H NMR spectra of (2-carboxyethyl)diphenylphosphine (black), 1·2HBr·H₂O (red) and H₄·2·2HBr·H₂O (blue) in DMSO-d₆.
Figure 3S. FTIR spectra of $\text{H}_4\cdot\text{1HBr}\cdot\text{H}_2\text{O}$ and $\text{H}_4\cdot\text{2HBr}\cdot\text{H}_2\text{O}$ compared with that of the ligands, i.e., (2-carboxyethyl)diphenylphosphine.
Table 15. Crystal data and experimental details for \([\text{Re}_6\text{Se}_8]\{\text{PPh}_2\text{CH}_2\text{CH}_2\text{COOH}\}_6]\text{Br}_2\cdot\text{6H}_2\text{O}\cdot\text{Et}_2\text{O}, \text{Na}_4[\{\text{Re}_6\text{Se}_8]\{\text{PPh}_2\text{CH}_2\text{CH}_2\text{COOH}\}_6] (\text{Na}_4\cdot\text{1}\cdot\text{4H}_2\text{O}), \text{and} \text{Na}_4[\{\text{Re}_6\text{Se}_8]\{\text{PPh}_2\text{CH}_2\text{CH}_2\text{COO}\}_6] (\text{Na}_4\cdot\text{2}\cdot\text{4H}_2\text{O}).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>H$_2$·2·2HBr·6H$_2$O·Et$_2$O</th>
<th>Na$_4$·1·4H$_2$O</th>
<th>Na$_4$·2·4H$_2$O</th>
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<td>C$<em>{90}$H$</em>{92}$Na$<em>4$O$</em>{16}$P$_6$Re$_6$Se$_8$</td>
<td>C$<em>{90}$H$</em>{92}$Na$<em>4$O$</em>{16}$P$_6$Re$_6$Se$_8$</td>
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<td>150(2)</td>
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<td>13.9958(3)</td>
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<td>b (Å)</td>
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<td>β (º)</td>
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<td>γ (º)</td>
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<td>Crystal size (mm)</td>
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<td>–17 ≤ h ≤ 17</td>
<td>–18 ≤ h ≤ 18</td>
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<td>Goodness-of-fit (GOF) on F$^2$</td>
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<tr>
<td>$R_I^2 / wR_I^b$ [I &gt; 2σ(I)]</td>
<td>0.0355/0.0979</td>
<td>0.0192/0.0464</td>
<td>0.0205/0.0467</td>
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<tr>
<td>$R_E^2 / wR_E^b$ (all data)</td>
<td>0.0433/0.1034</td>
<td>0.0215/0.0472</td>
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<tr>
<td>$\Delta\rho_{max}/\Delta\rho_{min}$ (e·Å$^{-3}$)</td>
<td>1.986/–1.316</td>
<td>1.274/–1.004</td>
<td>1.631/–1.037</td>
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Table 2S. Selected interatomic distances (Å) for [(Re₆Se₈)(PPh₂CH₂CH₂COOH)₆]Br₂·6H₂O·Et₂O (H₄-2·2HBr·6H₂O·Et₂O), Na₄[(Re₆Se₈)(PPh₂CH₂CH₂COO)₆]·4H₂O (Na₄-1·4H₂O), and Na₄[(Re₆Se₈)(PPh₂CH₂CH₂COO)₆]·4H₂O (Na₄-2·4H₂O).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Re–Re (Å)</th>
<th>Re–Q (Å)</th>
<th>Re–P (Å)</th>
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<tr>
<td>H₄-2·2HBr·6H₂O·Et₂O</td>
<td>2.6389(4)–2.6455(4)</td>
<td>2.5060(7)–2.5244(6)</td>
<td>2.4807(15)</td>
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<tr>
<td>Na₄-1·4H₂O</td>
<td>2.60495(16)–2.61506(15)</td>
<td>2.3864(7)–2.4129(7)</td>
<td>2.4842(8)–2.4913(7)</td>
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<tr>
<td>Na₄-2·4H₂O</td>
<td>2.6363(3)–2.6515(3)</td>
<td>2.4994(4)–2.5269(4)</td>
<td>2.4849(8)–2.4909(8)</td>
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</table>

Figure 4S. Layers parallel to the ab plane observed in the H₄-2·2HBr·6H₂O·Et₂O structure.
Figure 5S. Hydrogen bonds observed in the H₄-2HBr·6H₂O·Et₂O structure.

Figure 6S. Hydrogen bonds observed in the H₄-2HBr·6H₂O·Et₂O structure.
Figure 7S. HR-ESI-MS of Na₄·1·18H₂O in water (black) and corresponding simulations of {Na₄[[Re₆Se₆](PPh₂CH₂CH₂COO)]₆}⁴⁻⁻⁻ (x = 0, m/z = 729.4872; x = 1, m/z = 980.3126; x = 2, m/z = 1481.9633) (coloured).

Figure 8S. HR-ESI-MS of Na₄·2·16H₂O in water (black) and a simulation of cluster forms Na₄[[Re₆Se₆](PPh₂CH₂CH₂COO)]₆}⁴⁻⁻⁻ (x = 0 (m/z = 823.3777), 1 (m/z = 1105.4996)) and 2 (m/z = 1669.7442) (coloured).
Figure 9S. $^1$H NMR spectra of (2-carboxyethyl)diphenylphosphine sodium salt (black), Na$_4$-1·18H$_2$O (red) and Na$_4$-2·16H$_2$O (blue) in D$_2$O.

Figure 10S. FTIR spectra of Na$_4$-1·18H$_2$O and Na$_4$-2·16H$_2$O compared with that of the ligands, i.e., (2-carboxyethyl)diphenylphosphine.
Figure 11S. Non-porous 3D-coordination polymer based on octahedral clusters and alkali metals observed in the Na₄·1·4H₂O and Na₄·2·4H₂O structures.

Table 3S. The Na–O and hydrogen bond lengths in Na₄·1·4H₂O and Na₄·2·4H₂O.

<table>
<thead>
<tr>
<th>Contact</th>
<th>Na₄·1·4H₂O (Å)</th>
<th>Na₄·2·4H₂O (Å)</th>
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<tbody>
<tr>
<td>O1W···O212</td>
<td>2.774</td>
<td>2.771</td>
</tr>
<tr>
<td>O2W···O311</td>
<td>2.804</td>
<td>2.825</td>
</tr>
<tr>
<td>O1W···O2W</td>
<td>2.764 and 2.890</td>
<td>2.780 and 2.895</td>
</tr>
<tr>
<td>Na1···O111</td>
<td>2.297</td>
<td>2.289</td>
</tr>
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<td>Na1···O112</td>
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<td>Na1···O211</td>
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<td>Na1···O312</td>
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<td>Na2···O312</td>
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Figure 12S. Emission spectra of acetonitrile solutions of H$_4$-1·2HBr·H$_2$O (black line) and H$_4$-2·2HBr·H$_2$O (red line) under oxygen-free conditions.

Figure 13S. Luminescence decay curves of powdered H$_4$-1·2HBr·H$_2$O (black line) and H$_4$-2·2HBr·H$_2$O (red line).
Figure 14S. Luminescence decay curves of aerated (left) and deaerated (right) acetonitrile solutions of H$_4$-1·2HBr·H$_2$O (black line) and H$_4$-2·2HBr·H$_2$O (red line).

Figure 15S. Luminescence spectra of H$_4$-1·2HBr·H$_2$O in argon- (a) and oxygen-saturated (b) PBS.

Figure 16S. Luminescence spectra of H$_4$-2·2HBr·H$_2$O in argon- (a) and oxygen-saturated (b) PBS.
Figure 17S. Luminescence decay curves of H₄-1·2HBr·H₂O recorded at 720 nm in argon- (a) and oxygen-saturated (b) PBS.

Figure 18S. Luminescence decay curves of H₄-2·2HBr·H₂O recorded at 765 nm in argon- (a) and oxygen-saturated (b) PBS.
Figure 19S. Photoluminescence and X-ray excited optical luminescence (XEOL) spectra of H₄-1·2HBr·H₂O (A) and H₄-2·2HBr·H₂O (B) powders.

Figure 20S. Fragment of HR-ESI-MS of H₄-1·2HBr in ethanol containing HBr (black) and corresponding simulation (coloured). R¹ = CH₂CH₂COOH, R² = CH₂CH₂COOEt. Measured m/z values correspond to theoretical values: 1476.0116, 1490.0273 and 1504.0429 from left to right.
Figure 21S. Fragment of HR-ESI-MS of H₄·2·HBr in ethanol containing HBr (black) and corresponding simulation (coloured). R¹ = CH₂CH₂COOH, R² = CH₂CH₂COOEt. Measured m/z values correspond to theoretical values: 1677.8082, 1691.8239, 1705.8396 from left to right.

Figure 22S. TGA curves of H₄·1·2HBr·H₂O and H₄·2·2HBr·H₂O. Heating rates are 10° C·min⁻¹.
Figure 23S. TGA curves of Na₄·1·18H₂O and Na₄·2·16H₂O. Heating rates are 10° C·min⁻¹.

Figure 24S. FTIR spectra of Na₄·1·4H₂O and Na₄·2·4H₂O compared with that of the ligands, i.e., (2-carboxyethyl)diphenylphosphine.
Figure 25S. TGA curves of Na$_4$-1·4H$_2$O and Na$_4$-2·4H$_2$O. Heating rates of 10° C·min$^{-1}$. 