Supplementary Materials: Charge-assisted hydrogen-bonded networks of NH$_4^+$ and [Co(NH$_3$)$_6$]$^{3+}$ with the new linker anion of 4-phosphono-biphenyl-4’-carboxylic acid

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Figure S1. Photographs of crystals of (a) NH$_4$(HO$_3$P-(C$_6$H$_4$)$_2$-COOH)(H$_2$O$_3$P-(C$_6$H$_4$)$_2$-COOH), 1 and (b) [Co(NH$_3$)$_6$](O$_3$P-(C$_6$H$_4$)$_2$-COO)$\cdot4$H$_2$O, 2 taken with a light microscope.

Figure S2. FT-IR (ATR) spectrum of NH$_4$(HO$_3$P-(C$_6$H$_4$)$_2$-COOH)(H$_2$O$_3$P-(C$_6$H$_4$)$_2$-COOH), 1.
Figure S3. FT-IR (ATR) spectrum of [Co(NH₃)₆](O₃P-(C₆H₄)₂-COO)·4H₂O, 2.

Figure S4. Comparison of the experimental PXRD pattern of 1 (black) with the simulated pattern from the X-ray data (red). An additional comparison of the experimental powder pattern with the experimental pattern of the linker 4-phosphono-biphenyl-4’-carboxylic acid, BPPA shows, that there is a contribution of the linker in the measured pattern.

Packing Analyses

Despite the presence of biphenyl π-systems in compounds 1 and 2, there are no π–π interactions [1] and only few intermolecular C–H···π [2–5] evident.

The supramolecular packing analyses of the biphenyl rings are tabulated below (Tables S1 and S2).

The listed “Analysis of Short Ring-Interactions” for possible π-stacking interactions yielded rather rather long centroid-centroid distances (>4.0 Å) together with non-parallel ring planes (alpha >> 0°) and large slip angles (β, γ > 30°).

In comparison, significant π-stackings show rather short centroid-centroid contacts (<3.8 Å), near parallel ring planes (alpha < 10° to ~0° or even exactly 0° by symmetry), small slip angles
(β, γ < 25°) and vertical displacements (slippage < 1.5 Å) which translate into a sizable overlap of the aryl-plane areas [1,6–11].

Significant intermolecular C-H···π contacts start around 2.7 Å for the (C–)H···ring centroid distances with H-perp also starting at 2.6–2.7 Å and C–H···Cg > 145° [2–5,12–16].

Scheme S1. Graphical presentation of the parameters used for the description of CH–π interactions.

Packing Analysis for compound NH4(HO3P–(C6H4)2–COOH)(H2O3P–(C6H4)2–COOH), 1 for possible CH–π interactions (see Scheme S1 for explanation):

<table>
<thead>
<tr>
<th>X-H(I)</th>
<th>Res(I)</th>
<th>Cg(J)</th>
<th>[ARU(J)]</th>
<th>H-Cg</th>
<th>H-Perp</th>
<th>Gamma</th>
<th>C-H-Cg</th>
<th>C-Cg</th>
<th>X-H,π</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(2)-H(2A) [1]</td>
<td>Cg(3)</td>
<td>[1445.01]</td>
<td>2.94</td>
<td>2.91</td>
<td>7.42</td>
<td>137</td>
<td>3.684(3)</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>C(9)-H(9A) [1]</td>
<td>Cg(6)</td>
<td>[1555.01]</td>
<td>2.91</td>
<td>-2.88</td>
<td>7.85</td>
<td>135</td>
<td>3.638(3)</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>C(15)-H(15) [1]</td>
<td>Cg(3)</td>
<td>[1565.01]</td>
<td>2.91</td>
<td>-2.83</td>
<td>13.23</td>
<td>126</td>
<td>3.551(3)</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>Min or Max</td>
<td></td>
<td></td>
<td>2.910</td>
<td>-2.880</td>
<td>7.42</td>
<td>137.00</td>
<td>3.551</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

[1445] = -1 + X, -1 + Y, Z
[1555] = X, Y, Z
[1565] = X, 1 + Y, Z

The Cg(I) refer to the Ring Centre-of-Gravity numbers given in

Ring 3: C1-C2-C3-C4-C5-C6
Ring 5: C14-C15-C16-C17-C18-C19
Ring 6: C20-C21-C22-C23-C24-C25

Packing Analysis for compound [Co(NH3)6](O3P–(C6H4)2–COO)·4H2O, 2 for possible N–H···π, O–H···π, CH–π interactions (see Scheme S1 for explanation):

Analysis of X-H..Cg(π-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma < 30.0 Deg)
-Cg(J) = Center of gravity of ring J (Plane number above)
-H-Perp = Perpendicular distance of H to ring plane J
-Gamma = Angle between Cg-H vector and ring J normal
-X-H..Cg = X-H-Cg angle (degrees)
-X..Cg = Distance of X to Cg (Angstrom)
-X-H, π = Angle of the X-H bond with the π-plane (i.e., Perpendicular = 90 degrees, Parallel = 0 degrees)

<table>
<thead>
<tr>
<th>X-H(I)</th>
<th>Res(I)</th>
<th>Cg(J)</th>
<th>[ARU(I)]</th>
<th>H-Cg</th>
<th>H-Perp</th>
<th>Gamma</th>
<th>C-H..Cg</th>
<th>C..Cg</th>
<th>X-H, π</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(3)-H(3A)</td>
<td>[2]</td>
<td>-Cg(1)</td>
<td>1655.01</td>
<td>2.94(5)</td>
<td>-2.78</td>
<td>18.99</td>
<td>151(4)</td>
<td>3.672(3)</td>
<td>44</td>
</tr>
<tr>
<td>O(6)-H(6D)</td>
<td>[3]</td>
<td>-Cg(2)</td>
<td>4554.01</td>
<td>2.69(5)</td>
<td>2.51</td>
<td>20.96</td>
<td>139(4)</td>
<td>3.395(4)</td>
<td>43</td>
</tr>
<tr>
<td>C(11)-H(11)</td>
<td>[1]</td>
<td>-Cg(1)</td>
<td>4454.01</td>
<td>2.766(3)</td>
<td>2.73</td>
<td>9.36</td>
<td>137.5(3)</td>
<td>3.525(3)</td>
<td>38</td>
</tr>
</tbody>
</table>

Min or Max 2.690 −2.780 9.36 151.00 3.395 44

[1655] = 1 + X, Y, Z
[4554] = 1/2 + X, 1/2 −Y, −1/2 + Z
[4454] = −1/2 + X, 1/2 −Y, −1/2 + Z

The Cg(I) refer to the Ring Centre-of-Gravity numbers given in

Ring 1: C1-C2-C3-C4-C5-C6
Ring 2: C7-C8-C9-C10-C11-C12

References


