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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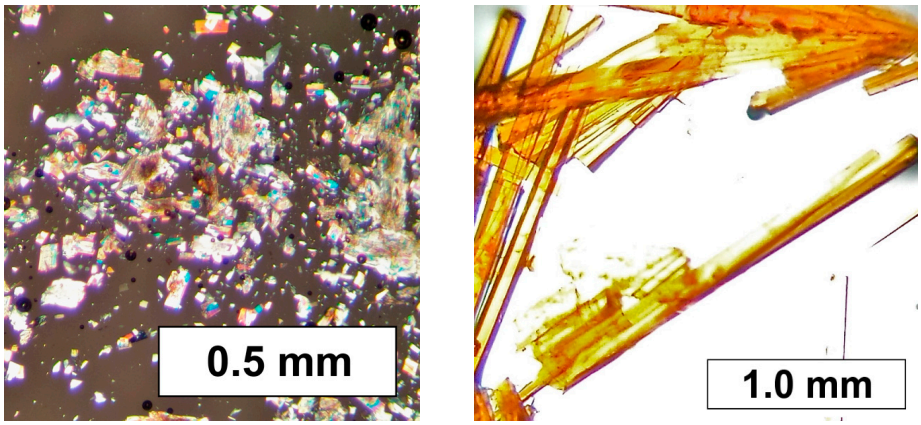


Figure S1. Photographs of crystals of (**a**) $NH_4(HO_3P\text{-}(C_6H_4)_2\text{-}COOH)(H_2O_3P\text{-}(C_6H_4)_2\text{-}COOH)$, **1** and (**b**) $[Co(NH_3)_6](O_3P\text{-}(C_6H_4)_2\text{-}COO)\cdot 4H_2O$, **2** taken with a light microscope.

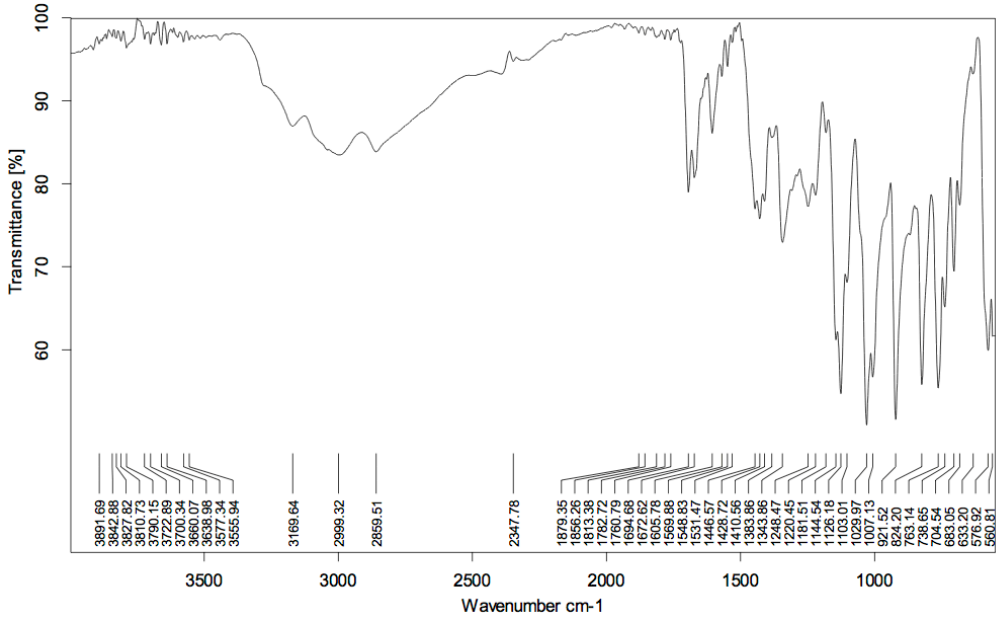


Figure S2. FT-IR (ATR) spectrum of $NH_4(HO_3P\text{-}(C_6H_4)_2\text{-}COOH)(H_2O_3P\text{-}(C_6H_4)_2\text{-}COOH)$, **1**.

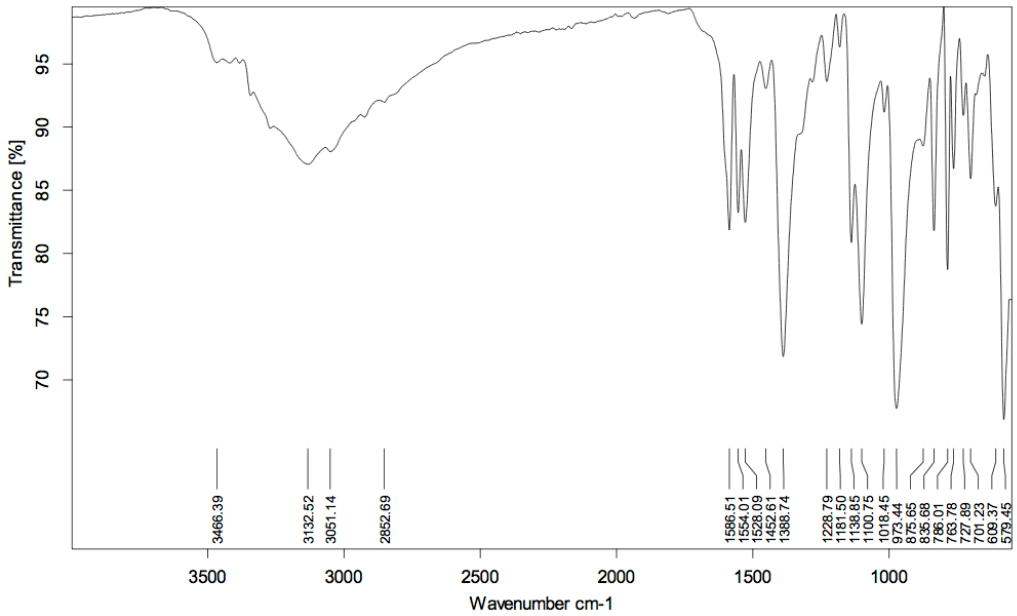


Figure S3. FT-IR (ATR) spectrum of $[Co(NH_3)_6](O_3P\text{-}(C_6H_4)_2\text{-}COO)\cdot 4H_2O$, **2**.

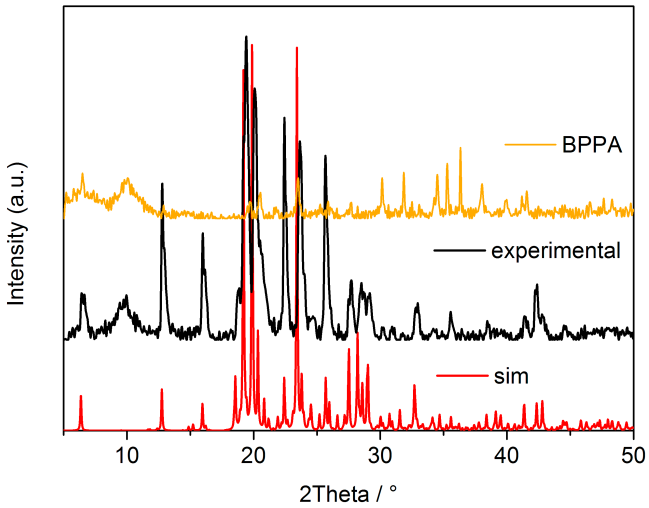


Figure S4. Comparison of the experimental PXRD pattern of **1** (black) with the simulated pattern from the X-ray data (red). An additional comparison of the experimental powder pattern with the experimental pattern of the linker 4-phosphono-biphenyl-4′-carboxylic acid, BPPA shows, that there is a contribution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

Packing Analyses

Packing Analysis by PLATON ((a) A. Spek, *Acta Crystallographica Section D*, **2009**, *65*, 148–155; (b) A.L. Spek *PLATON—A multipurpose crystallographic tool*, Utrecht University: Utrecht, The Netherlands, 2005.)

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.

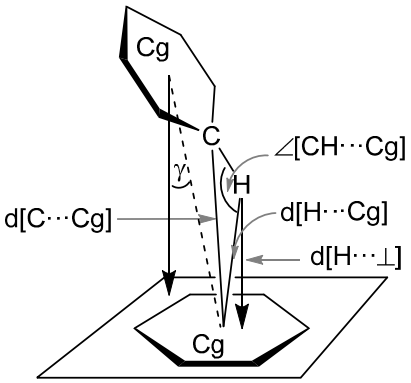
The supramolecular packing analyses of the biphenyl rings are tabulated below (Tables S1 and S2).

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 $NH_4(HO_3P–(C_6H_4)_2–COOH)(H_2O_3P–(C_6H_4)_2–COOH)$, **1** for possible **CH–π interactions** (see Scheme S1 for explanation)**:**

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Analysis of X-H..Cg(π-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma < 30.0 Deg)

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-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)

X--H(I)	Res(I)	Cg(J)	[ARU(J)]	H..Cg	H-Perp	Gamma	C-H..Cg	C..Cg	X-H,π
C(2)-H(2A)	[1]	->Cg(5)	[1445.01]	2.94	2.91	7.42	137	3.684(3)	50
C(9)-H(9A)	[1]	->Cg(6)	[1555.01]	2.91	−2.88	7.85	135	3.638(3)	48
C(15)-H(15)	[1]	->Cg(3)	[1565.01]	2.91	−2.83	13.23	126	3.551(3)	49
			Min or Max	2.910	−2.880	7.42	137.00	3.551	50

[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 $[Co(NH_3)_6](O_3P–(C_6H_4)_2–COO)·4H_2O$, **2** for possible **N–H···π, O–H···π, CH–π interactions** (see Scheme S1 for explanation)**:**

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Analysis of X-H...Cg(Pi-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)

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

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