

Supplementary Materials: Charge-assisted hydrogen-bonded networks of NH_4^+ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ with the new linker anion of 4-phosphono-biphenyl-4'-carboxylic acid

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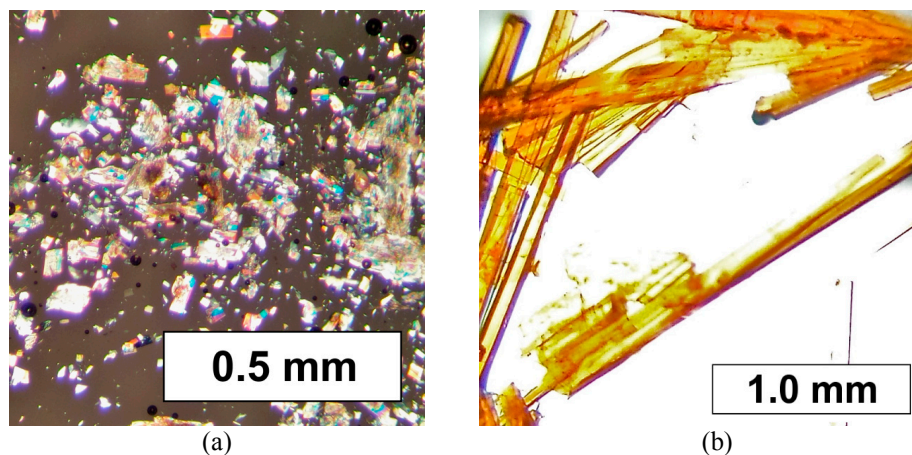


Figure S1. Photographs of crystals of (a) $\text{NH}_4(\text{HO}_3\text{P}-(\text{C}_6\text{H}_4)_2-\text{COOH})(\text{H}_2\text{O}_3\text{P}-(\text{C}_6\text{H}_4)_2-\text{COOH})$, **1** and (b) $[\text{Co}(\text{NH}_3)_6](\text{O}_3\text{P}-(\text{C}_6\text{H}_4)_2-\text{COO})\cdot 4\text{H}_2\text{O}$, **2** taken with a light microscope.

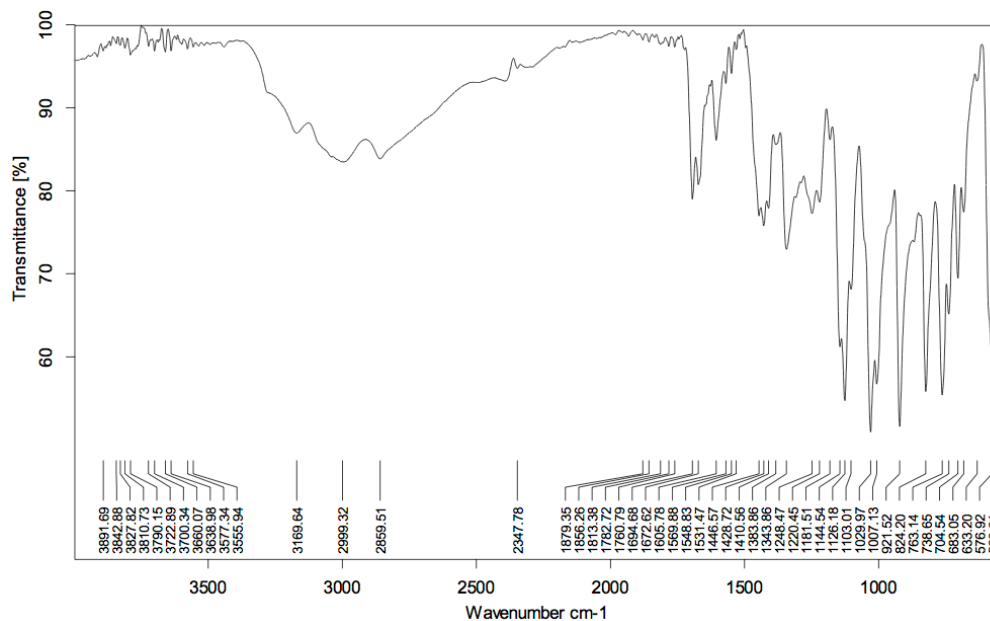


Figure S2. FT-IR (ATR) spectrum of $\text{NH}_4(\text{HO}_3\text{P}-(\text{C}_6\text{H}_4)_2-\text{COOH})(\text{H}_2\text{O}_3\text{P}-(\text{C}_6\text{H}_4)_2-\text{COOH})$, **1**.

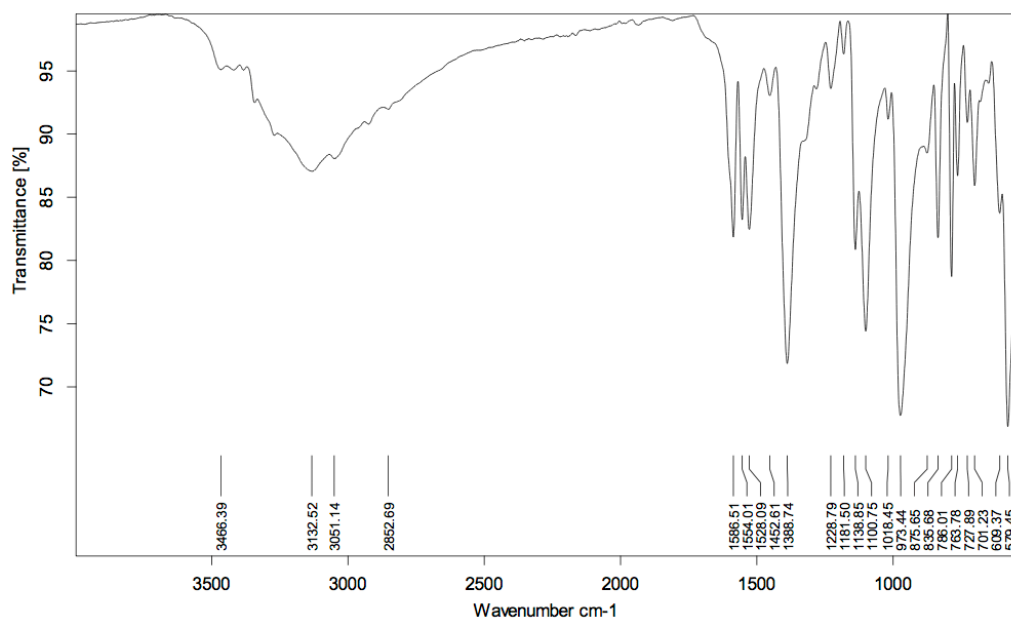


Figure S3. FT-IR (ATR) spectrum of $[\text{Co}(\text{NH}_3)_6](\text{O}_3\text{P}-(\text{C}_6\text{H}_4)_2-\text{COO})\cdot 4\text{H}_2\text{O}$, **2**.

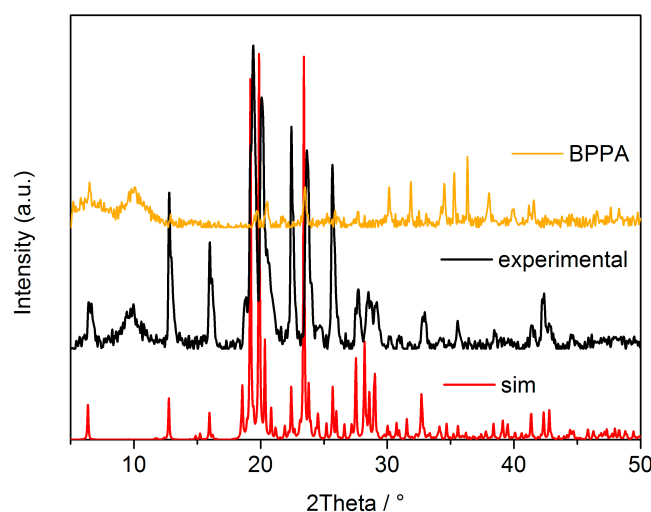


Figure S4. Comparison of the experimental PXRD pattern of **1** (black) with the simulated pattern from the X-ray data (red). An additional comparison of the experimental powder pattern with the experimental pattern of the linker 4-phosphono-biphenyl-4'-carboxylic acid, BPPA shows, that there is a contribution 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 \cdots π [2–5] evident.

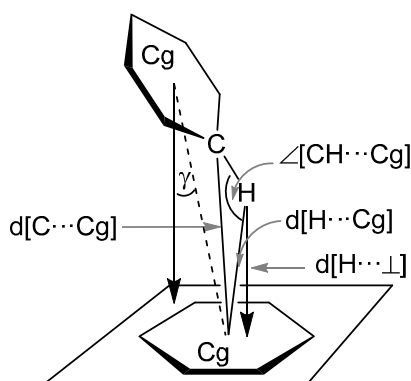
The supramolecular packing analyses of the biphenyl rings are tabulated below (Tables S1 and S2).

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 $\gg 0^\circ$) and large slip angles ($\beta, \gamma > 30^\circ$).

In comparison, significant π -stackings show rather short centroid-centroid contacts (<3.8 Å), near parallel ring planes (alpha $< 10^\circ$ to $\sim 0^\circ$ or even exactly 0° by symmetry), small slip angles

(β , $\gamma < 25^\circ$) and vertical displacements (slippage $< 1.5 \text{ \AA}$) which translate into a sizable overlap of the aryl-plane areas [1,6–11].

Significant intermolecular C–H $\cdots\pi$ contacts start around 2.7 \AA for the (C–)H \cdots ring centroid distances with H-perp also starting at $2.6\text{--}2.7 \text{ \AA}$ and C–H \cdots Cg $> 145^\circ$ [2–5,12–16].



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

Packing Analysis for compound $\text{NH}_4(\text{HO}_3\text{P}-(\text{C}_6\text{H}_4)_2-\text{COOH})(\text{H}_2\text{O}_3\text{P}-(\text{C}_6\text{H}_4)_2-\text{COOH})$, **1** for possible **CH- π interactions** (see Scheme S1 for explanation):

Analysis of X-H...Cg(π -Ring) Interactions (H...Cg $< 3.0 \text{ \AA}$. - Gamma $< 30.0 \text{ Deg}$)

-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
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 $[\text{Co}(\text{NH}_3)_6](\text{O}_3\text{P}-(\text{C}_6\text{H}_4)_2-\text{COO})\cdot 4\text{H}_2\text{O}$, **2** for possible **N-H $\cdots\pi$, O-H $\cdots\pi$, CH- π interactions** (see Scheme S1 for explanation):

Analysis of X-H...Cg(π -Ring) Interactions (H...Cg $< 3.0 \text{ \AA}$. - Gamma $< 30.0 \text{ Deg}$)

-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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