Electronic Supporting Information

An Unexpected Imidazole-Induced Porphyrinylphosphonate-Based MOF-to-HOF Structural Transformation Leading to the Enhancement of Proton Conductivity

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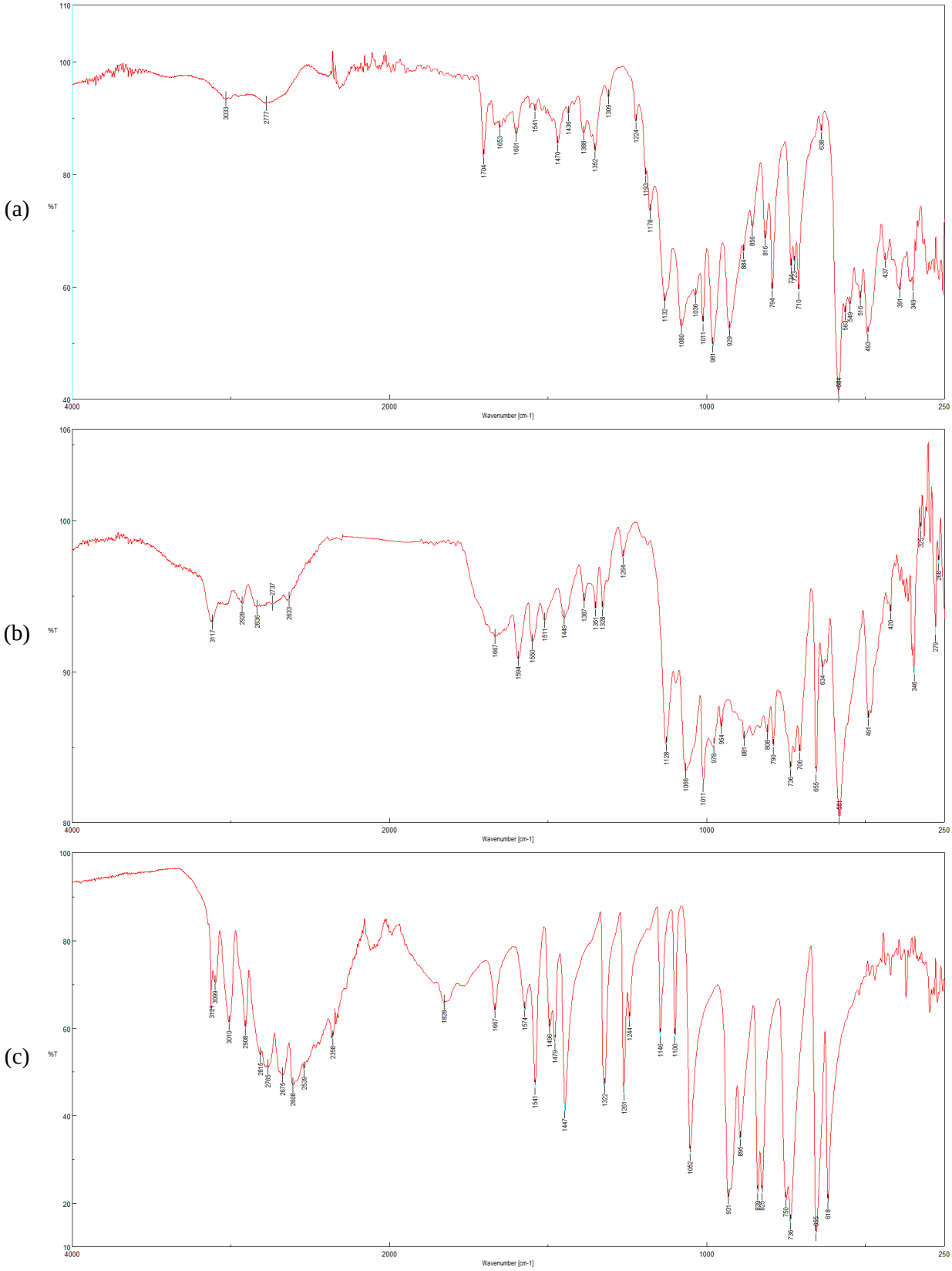


Figure S1. IR spectra of **IPCE-1Pd** – (a), **IPCE-1Pd_Im** – (b) and imidazole – (c).

Structural characterization of IPCE-1Pd

Table S1. Crystal data and structure refinement for **IPCE-1Pd**.

Identification code	**IPCE-1Pd**
CCDC number	2082843
Empirical formula	$[C_{44}H_{28}N_4O_{12}P_4PdZn_2 \cdot 2(C_3H_7NO) \cdot H_2O]$
Formula weight	1329.93
Wavelength, Å	1.5418
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	20.5052(18)
b, Å	25.899(2)
c, Å	5.2570(7)
β, º	93.923(11)
Volume, $Å^3$	2785.3(5)
Z	2
Dx, g cm^{-3}	1.588
2θmin – 2θmax, increment, °	4.000 – 70.000, 0.017
No. params/restraints	153/184
$R_p/R_{wp}/R_{exp}$	0.0393/0.0522/0.0267
Goodness-of-fit	1.954

Table S2. Bond lengths in **IPCE-1Pd**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Pd1	N2	2.029(11)	C17	P2	1.848(14)
Pd1	N2	2.029(11)	C18	C19	1.39(2)
Pd1	N1	2.059(11)	C18	H18	0.9300
Pd1	N1	2.059(11)	C19	H19	0.9300
N1	C1	1.366(17)	C20	C21	1.425(19)
N1	C20	1.391(19)	C20	C13	1.48(2)
N2	C9	1.385(17)	C21	C22	1.350(19)
N2	C12	1.400(19)	C21	H21	0.9301
C1	C2	1.413(19)	C22	H22	0.9300
C1	C22	1.425(19)	P1	O2	1.502(11)
C2	C9	1.48(2)	P1	O3	1.544(11)
C2	C3	1.50(2)	P1	O1	1.560(11)
C3	C8	1.37(2)	O1	Zn1	1.729(9)
C3	C4	1.400(19)	O2	Zn1	1.766(9)
C4	C5	1.39(2)	O3	H3	0.8200
C4	H4	0.9300	P2	O5	1.488(11)
C5	C6	1.43(2)	P2	O4	1.510(11)

C5	H5	0.9300	P2	O6	1.551(10)
C6	C7	1.358(19)	O4	Zn1	1.651(10)
C6	P1	1.770(14)	O5	Zn1	1.747(10)
C7	C8	1.419(19)	O6	H6	0.8200
C7	H7	0.9300	Zn1	O1	1.729(9)
C8	H8	0.9300	Zn1	O5	1.747(10)
C9	C10	1.49(2)	Zn1	O2	1.766(9)
C10	C11	1.355(19)	C23	N3	1.458(19)
C10	H10	0.9300	C23	H23A	0.9600
C11	C12	1.427(18)	C23	H23B	0.9600
C11	H11	0.9299	C23	H23C	0.9601
C12	C13	1.394(19)	N3	C24	1.333(18)
C13	C20	1.48(2)	N3	C25	1.450(19)
C13	C14	1.50(2)	C24	O7	1.282(16)
C14	C19	1.38(2)	C24	H24	0.9300
C14	C15	1.41(2)	C25	H25A	0.9600
C15	C16	1.366(19)	C25	H25B	0.9600
C15	H15	0.9300	C25	H25C	0.9599
C16	C17	1.43(2)	O8	H81	0.8569
C16	H16	0.9300	O8	H82	0.8506
C17	C18	1.39(2)			

Table S3. Bond angles in **IPCE-1Pd**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N2	Pd1	N2	180.000(2)	C18	C17	C16	115.3(12)
N2	Pd1	N1	90.3(4)	C18	C17	P2	131.6(12)
N2	Pd1	N1	89.7(4)	C16	C17	P2	112.7(10)
N2	Pd1	N1	89.7(4)	C19	C18	C17	122.4(14)
N2	Pd1	N1	90.3(4)	C19	C18	H18	118.8
N1	Pd1	N1	180.0(5)	C17	C18	H18	118.8
C1	N1	C20	102.8(11)	C14	C19	C18	121.2(13)
C1	N1	Pd1	129.4(9)	C14	C19	H19	119.4
C20	N1	Pd1	127.6(9)	C18	C19	H19	119.4
C9	N2	C12	105.5(10)	N1	C20	C21	111.3(12)
C9	N2	Pd1	126.3(9)	N1	C20	C13	124.4(12)
C12	N2	Pd1	128.2(8)	C21	C20	C13	123.2(13)
N1	C1	C2	123.3(13)	C22	C21	C20	106.9(12)
N1	C1	C22	112.6(12)	C22	C21	H21	126.6
C2	C1	C22	124.0(12)	C20	C21	H21	126.6

C1	C2	C9	124.9(13)	C21	C22	C1	105.9(12)
C1	C2	C3	118.2(12)	C21	C22	H22	127.1
C9	C2	C3	116.2(11)	C1	C22	H22	127.1
C8	C3	C4	117.7(12)	O2	P1	O3	113.6(7)
C8	C3	C2	121.2(12)	O2	P1	O1	112.4(6)
C4	C3	C2	120.7(13)	O3	P1	O1	107.2(6)
C5	C4	C3	121.4(14)	O2	P1	C6	111.2(6)
C5	C4	H4	119.3	O3	P1	C6	104.4(6)
C3	C4	H4	119.3	O1	P1	C6	107.5(7)
C4	C5	C6	120.2(13)	P1	O1	Zn1	143.3(7)
C4	C5	H5	119.9	P1	O2	Zn1	153.7(6)
C6	C5	H5	119.9	P1	O3	H3	109.5
C7	C6	C5	117.8(13)	O5	P2	O4	113.4(6)
C7	C6	P1	126.4(11)	O5	P2	O6	112.3(6)
C5	C6	P1	113.8(10)	O4	P2	O6	111.0(6)
C6	C7	C8	120.8(14)	O5	P2	C17	107.9(7)
C6	C7	H7	119.6	O4	P2	C17	108.1(7)
C8	C7	H7	119.6	O6	P2	C17	103.5(6)
C3	C8	C7	121.3(13)	P2	O4	Zn1	136.1(6)
C3	C8	H8	119.3	P2	O5	Zn1	165.1(7)
C7	C8	H8	119.3	P2	O6	H6	109.5
N2	C9	C2	125.6(12)	O4	Zn1	O1	101.1(5)
N2	C9	C10	107.1(11)	O4	Zn1	O5	112.8(5)
C2	C9	C10	126.8(12)	O1	Zn1	O5	94.4(5)
C11	C10	C9	109.3(12)	O4	Zn1	O2	131.4(5)
C11	C10	H10	125.3	O1	Zn1	O2	111.1(4)
C9	C10	H10	125.3	O5	Zn1	O2	100.3(5)
C10	C11	C12	105.0(12)	N3	C23	H23A	109.5
C10	C11	H11	127.5	N3	C23	H23B	109.5
C12	C11	H11	127.5	H23A	C23	H23B	109.5
C13	C12	N2	126.3(12)	N3	C23	H23C	109.5
C13	C12	C11	120.9(13)	H23A	C23	H23C	109.5
N2	C12	C11	112.1(11)	H23B	C23	H23C	109.5
C12	C13	C20	123.3(13)	C24	N3	C25	119.4(12)
C12	C13	C14	118.1(12)	C24	N3	C23	122.0(12)
C20	C13	C14	118.1(12)	C25	N3	C23	117.6(11)
C19	C14	C15	118.0(13)	O7	C24	N3	118.8(12)
C19	C14	C13	123.6(13)	O7	C24	H24	120.6
C15	C14	C13	118.3(13)	N3	C24	H24	120.6

C16	C15	C14	120.5(14)	N3	C25	H25A	109.5
C16	C15	H15	119.7	N3	C25	H25B	109.5
C14	C15	H15	119.7	H25A	C25	H25B	109.5
C15	C16	C17	122.3(13)	N3	C25	H25C	109.5
C15	C16	H16	118.8	H25A	C25	H25C	109.5
C17	C16	H16	118.8	H25B	C25	H25C	109.5
				H81	O8	H82	109.4

Table S4. Hydrogen bonds in **IPCE-1Pd**.

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
O3	H3	O4	0.82	1.92	2.711(13)	161
O6	H6	O7	0.82	2.29	3.065(13)	159
O8	H81	O3	0.85	2.45	2.85(2)	110

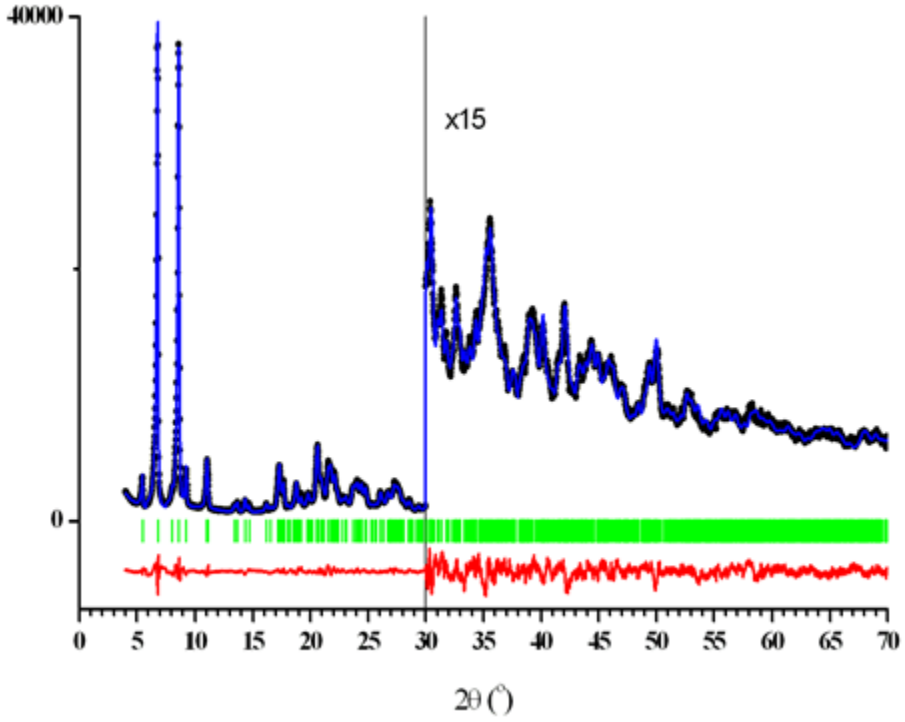


Figure S2. The Rietveld plot for **IPCE-1Pd** showing the experimental (black dots), calculated (blue) and difference (red) curves. The vertical green bars denote calculated positions of the diffraction peaks.

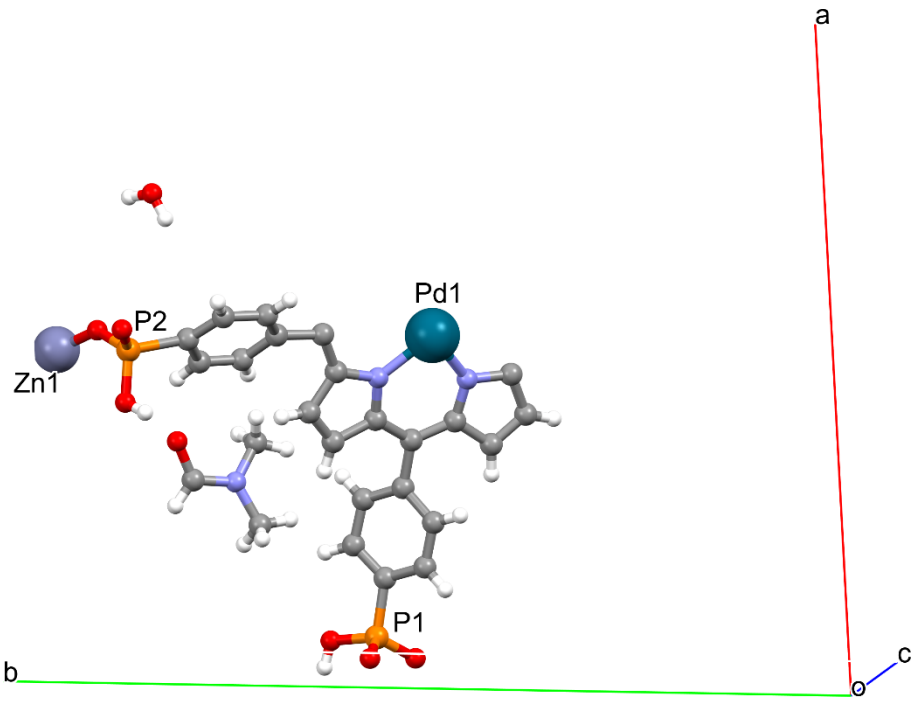


Figure S3. Asymmetric unit of **IPCE-1Pd**. (Pd: dark blue spheres, C: gray spheres, O: red spheres, N: blue spheres, P: orange spheres, H: white spheres).

Each of the four phosphonate groups is monodeprotonated and binds two zinc cations in the monodentate mode (**Figures S4, S5**). The P–O distances of the phosphonate groups of Pd-H_4TPPP^{4-} are within 1.488(11)–1.560(11) Å. The Zn(II) cations have tetrahedral coordination environment provided by binding with four phosphonate oxygen atoms [O1, O2, O4 and O5] from four palladium(II) porphyrinates, with the Zn–O bond lengths varying in range of 1.651(10)–1.766(9) Å and O-Zn-O angles ranging from 94.4(5)° to 131.4(5)°.

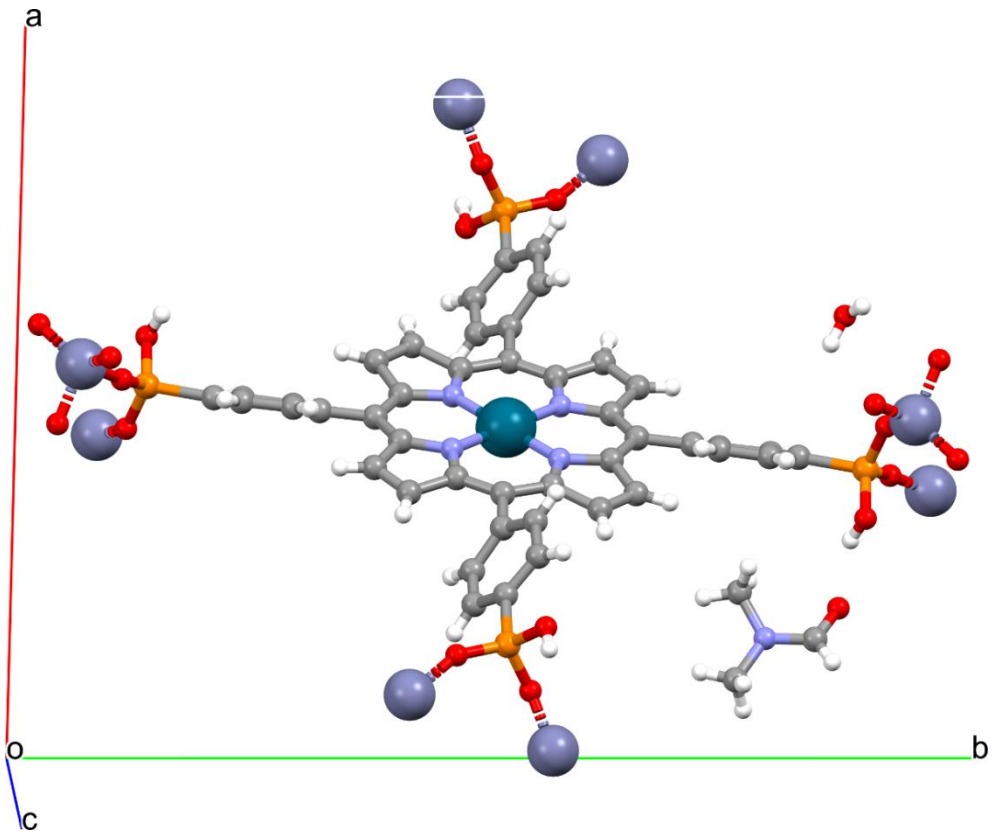


Figure S4. Coordination environment of palladium(II) porphyrinate in **IPCE-1Pd**.

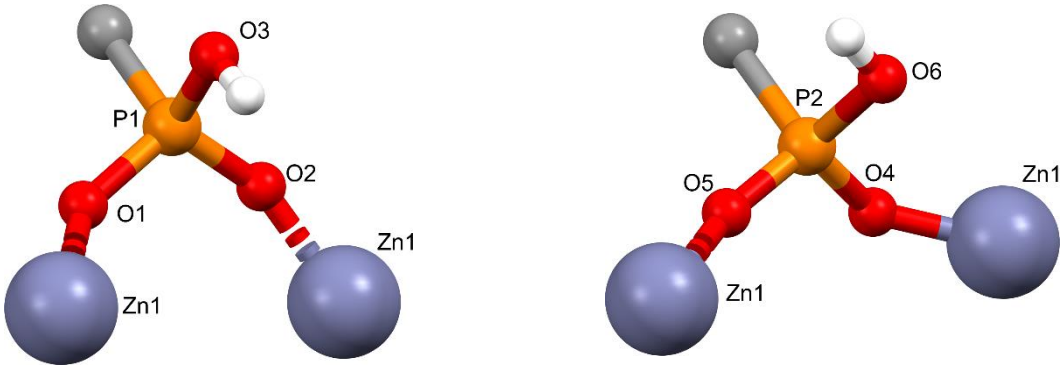


Figure S5. Graphical representation of the coordination modes of coordinated phosphonate groups in **IPCE-1Pd**.

Predictably, the smallest moiety of the secondary building unit of this MOF is a dimer formed by the interconnection of two nearest zinc atoms through two bridging phosphonate groups from different porphyrins [P1, O1, O2, O3] with the Zn···Zn distance of 4.450(5) Å, that is close to this binding mode in other MOFs based on porphyrinylphosphonates (**Figure S6**).[1–3]

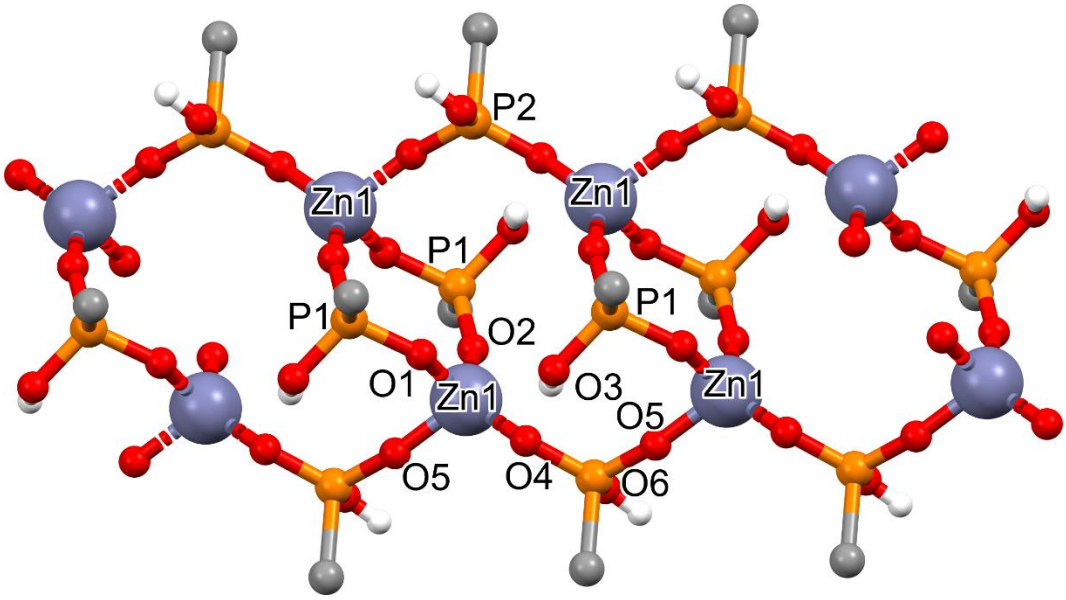


Figure S6. Graphical representation of the inorganic layer in the structure of **IPCE-1Pd**.

Further, the bonding of two dimers by two phosphonates [P2, O4, O5, O6] leads to the formation of a 1D inorganic layer, which is strengthened by the formation of strong intermolecular hydrogen bonds between oxygen atoms of neighboring porphyrin molecules (the O3…O4 distance is 2.711(13) Å).

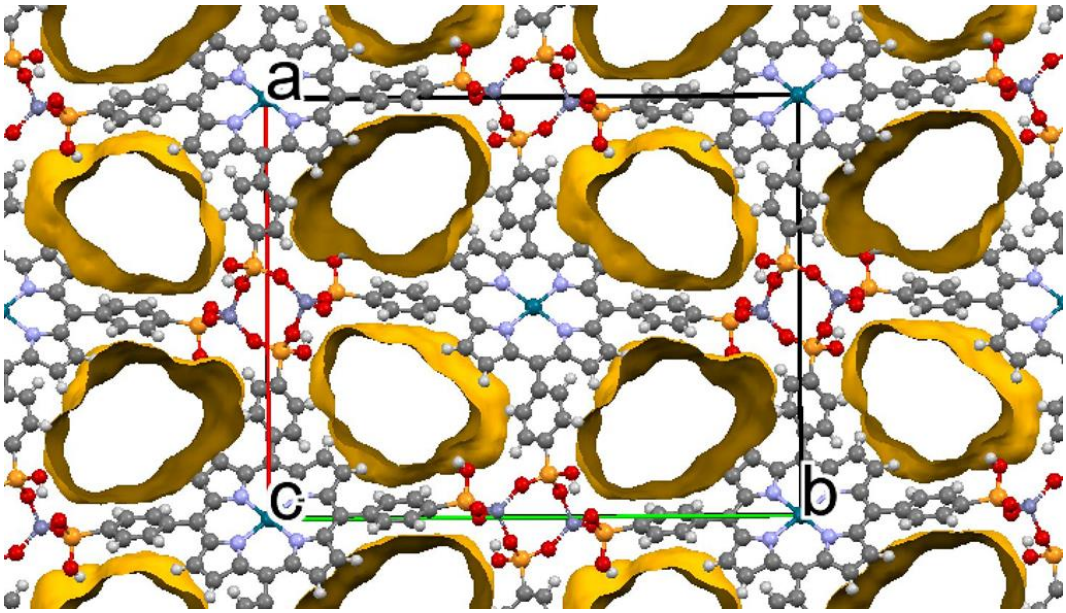


Figure S7. Channels in **IPCE-1Pd** viewed along the c axis. *dmf* and water molecules situated in the channels are not shown for clarity.

Structural characterization of IPCE-1Pd_Im

Table S5. Crystal data and structure refinement for **IPCE-1Pd_Im**.

Identification code	**IPCE-1Pd_Im**
CCDC number	2212074
Empirical formula	$[C_{62}H_{53}N_{16}O_{12}P_4PdZn_2]^+ \cdot C_3H_3N_2^- \cdot 0.6(C_3H_4N_2) \cdot 2.2H_2O$
Formula weight	1720.56
Wavelength, Å	1.5418
Crystal system	monoclinic
Space group	C2/c
a, Å	19.1484(17)
b, Å	34.587(2)
c, Å	12.4658(12)
β, °	120.124(19)
Volume, $Å^3$	7140.9(15)
Z	4
Dx, g cm^{-3}	1.600
2θmin – 2θmax, increment, °	4.508 – 70.009, 0.017
No. params/restraints	220/240
$R_p/R_{wp}/R_{exp}$	0.0227/0.0328/0.0130
goodness-of-fit	2.521

Table S6. Bond lengths in **IPCE-1Pd_Im**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Pd1	N1	2.021(9)	O2	H2	0.8200
Pd1	N1	2.021(9)	O3	H3	0.8200
Pd1	N2	2.069(8)	P2	O4	1.500(9)
Pd1	N2	2.069(8)	P2	O5	1.512(9)
N1	C1	1.368(15)	P2	O6	1.562(11)
N1	C20	1.374(11)	O5	H5A	0.8200
N2	C12	1.372(11)	O6	H6	0.8200
N2	C9	1.397(16)	Zn1	N5	1.942(8)
C1	C2	1.384(12)	Zn1	N3	1.990(10)
C1	C22	1.471(14)	Zn1	N7	2.030(10)
C2	C9	1.425(14)	N3	C23	1.327(15)
C2	C3	1.513(17)	N3	C25	1.396(16)
C3	C8	1.372(16)	C23	N4	1.310(16)
C3	C4	1.394(17)	C23	H23	0.9300
C4	C5	1.408(15)	N4	C24	1.414(15)
C4	H4	0.9300	N4	H4A	0.8599

C5	C6	1.382(17)	C24	C25	1.360(17)
C5	H5	0.9300	C24	H24	0.9299
C6	C7	1.391(17)	C25	H25	0.9300
C6	P1	1.804(13)	N5	C26	1.340(15)
C7	C8	1.425(15)	N5	C28	1.395(18)
C7	H7	0.9300	C26	N6	1.320(15)
C8	H8	0.9300	C26	H26	0.9300
C9	C10	1.470(13)	N6	C27	1.356(18)
C10	C11	1.326(15)	C27	C28	1.312(14)
C10	H10	0.9300	C27	H27	0.9300
C11	C12	1.451(14)	C28	H28	0.9300
C11	H11	0.9300	N7	C29	1.312(19)
C12	C13	1.393(15)	N7	C31	1.339(13)
C13	C20	1.414(15)	C29	N8	1.364(16)
C13	C14	1.518(11)	C29	H29	0.9300
C14	C19	1.376(18)	N8	C30	1.377(13)
C14	C15	1.396(17)	N8	H8A	0.8600
C15	C16	1.391(12)	C30	C31	1.332(18)
C15	H15	0.9300	C30	H30	0.9300
C16	C17	1.388(18)	C31	H31	0.9300
C16	H16	0.9300	C32	N9	1.327(12)
C17	C18	1.358(18)	C32	N9	1.327(12)
C17	P2	1.814(9)	C32	H32	0.9300
C18	C19	1.411(12)	N9	C33	1.392(13)
C18	H18	0.9300	C33	C33	1.45(2)
C19	H19	0.9300	C33	H33	0.9300
C20	C13	1.414(15)	N10	C34	1.33(4)
C20	C21	1.495(16)	N10	C36	1.36(5)
C21	C22	1.319(14)	N10	H10A	0.8599
C21	H21	0.9300	C34	N11	1.29(6)
C22	H22	0.9300	C34	H34	0.9297
P1	O2	1.490(7)	N11	C35	1.38(4)
P1	O1	1.521(10)	C35	C36	1.35(6)
P1	O3	1.542(8)	C35	H35	0.9297
O1	Zn1	1.942(8)	C36	H36	0.9298

Table S7. Bond angles in **IPCE-1Pd_Im**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N1	Pd1	N1	180.0(3)	O1	P1	C6	103.9(5)
N1	Pd1	N2	93.0(3)	O3	P1	C6	106.8(4)

N1	Pd1	N2	87.0(3)	P1	O1	Zn1	144.9(4)
N1	Pd1	N2	87.0(3)	P1	O2	H2	109.5
N1	Pd1	N2	93.0(3)	P1	O3	H3	109.5
N2	Pd1	N2	180.0(6)	O4	P2	O5	112.0(5)
C1	N1	C20	107.7(9)	O4	P2	O6	108.3(5)
C1	N1	Pd1	128.0(5)	O5	P2	O6	108.9(5)
C20	N1	Pd1	124.3(8)	O4	P2	C17	107.2(5)
C12	N2	C9	105.4(8)	O5	P2	C17	116.5(5)
C12	N2	Pd1	123.7(7)	O6	P2	C17	103.5(5)
C9	N2	Pd1	130.3(6)	P2	O5	H5A	109.5
N1	C1	C2	128.7(9)	P2	O6	H6	109.5
N1	C1	C22	109.0(7)	N5	Zn1	O1	112.8(4)
C2	C1	C22	122.1(11)	N5	Zn1	N3	112.2(3)
C1	C2	C9	123.1(11)	O1	Zn1	N3	107.2(4)
C1	C2	C3	118.6(9)	N5	Zn1	N7	106.6(4)
C9	C2	C3	117.2(9)	O1	Zn1	N7	111.1(3)
C8	C3	C4	118.6(11)	N3	Zn1	N7	106.7(4)
C8	C3	C2	122.3(11)	C23	N3	C25	106.7(10)
C4	C3	C2	118.8(10)	C23	N3	Zn1	130.4(9)
C3	C4	C5	121.5(11)	C25	N3	Zn1	122.7(8)
C3	C4	H4	119.3	N4	C23	N3	111.1(11)
C5	C4	H4	119.3	N4	C23	H23	124.4
C6	C5	C4	119.8(12)	N3	C23	H23	124.4
C6	C5	H5	120.1	C23	N4	C24	108.3(10)
C4	C5	H5	120.1	C23	N4	H4A	125.9
C5	C6	C7	119.3(11)	C24	N4	H4A	125.9
C5	C6	P1	119.7(9)	C25	C24	N4	105.2(10)
C7	C6	P1	121.0(9)	C25	C24	H24	127.4
C6	C7	C8	120.3(11)	N4	C24	H24	127.4
C6	C7	H7	119.8	C24	C25	N3	108.3(11)
C8	C7	H7	119.8	C24	C25	H25	125.9
C3	C8	C7	120.4(11)	N3	C25	H25	125.9
C3	C8	H8	119.8	C26	N5	C28	103.5(9)
C7	C8	H8	119.8	C26	N5	Zn1	131.0(9)
N2	C9	C2	122.2(9)	C28	N5	Zn1	124.6(7)
N2	C9	C10	108.5(9)	N6	C26	N5	111.2(12)
C2	C9	C10	129.3(11)	N6	C26	H26	124.4
C11	C10	C9	108.1(10)	N5	C26	H26	124.4
C11	C10	H10	126.0	C26	N6	C27	106.9(10)
C9	C10	H10	126.0	C28	C27	N6	107.4(11)
C10	C11	C12	106.8(8)	C28	C27	H27	126.3

C10	C11	H11	126.6	N6	C27	H27	126.3
C12	C11	H11	126.6	C27	C28	N5	108.9(12)
N2	C12	C13	125.4(9)	C27	C28	H28	125.6
N2	C12	C11	111.0(9)	N5	C28	H28	125.6
C13	C12	C11	123.5(8)	C29	N7	C31	102.0(10)
C12	C13	C20	127.4(9)	C29	N7	Zn1	129.6(7)
C12	C13	C14	116.5(9)	C31	N7	Zn1	127.1(9)
C20	C13	C14	114.7(9)	N7	C29	N8	111.3(9)
C19	C14	C15	119.7(8)	N7	C29	H29	124.3
C19	C14	C13	121.4(10)	N8	C29	H29	124.3
C15	C14	C13	118.4(11)	C29	N8	C30	107.3(11)
C16	C15	C14	120.7(12)	C29	N8	H8A	126.3
C16	C15	H15	119.6	C30	N8	H8A	126.3
C14	C15	H15	119.6	C31	C30	N8	101.2(8)
C17	C16	C15	118.8(11)	C31	C30	H30	129.4
C17	C16	H16	120.6	N8	C30	H30	129.4
C15	C16	H16	120.6	C30	C31	N7	115.2(11)
C18	C17	C16	120.9(8)	C30	C31	H31	122.4
C18	C17	P2	121.6(10)	N7	C31	H31	122.4
C16	C17	P2	117.2(9)	N9	C32	N9	110.4(14)
C17	C18	C19	120.6(12)	N9	C32	H32	124.8
C17	C18	H18	119.7	N9	C32	H32	124.8
C19	C18	H18	119.7	C32	N9	C33	109.2(9)
C14	C19	C18	119.2(11)	N9	C33	C33	104.9(6)
C14	C19	H19	120.4	N9	C33	H33	127.6
C18	C19	H19	120.4	C33	C33	H33	127.6
N1	C20	C13	125.9(10)	C34	N10	C36	107(3)
N1	C20	C21	108.1(9)	C34	N10	H10A	126.3
C13	C20	C21	125.9(8)	C36	N10	H10A	126.3
C22	C21	C20	107.2(8)	N11	C34	N10	112(3)
C22	C21	H21	126.4	N11	C34	H34	124.0
C20	C21	H21	126.4	N10	C34	H34	124.0
C21	C22	C1	108.0(10)	C34	N11	C35	106(3)
C21	C22	H22	126.0	C36	C35	N11	108(4)
C1	C22	H22	126.0	C36	C35	H35	125.8
O2	P1	O1	113.5(4)	N11	C35	H35	125.8
O2	P1	O3	111.0(5)	C35	C36	N10	106(3)
O1	P1	O3	111.0(4)	C35	C36	H36	127.0
O2	P1	C6	110.3(5)	N10	C36	H36	127.0

Table S8. Hydrogen bonds in **IPCE-1Pd_Im**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N4	H4A	O4	0.86	2.01	2.785(13)	149.00
O2	H2	O3	0.82	2.25	2.562(10)	103.00
O3	H3	N6	0.82	2.32	3.120(11)	166.00
O5	H5A	O5	0.82	1.70	2.473(10)	157.00
O6	H6	N9	0.82	2.04	2.845(9)	167.00
N8	H8A	O1W	0.86	2.34	2.697(13)	105.00

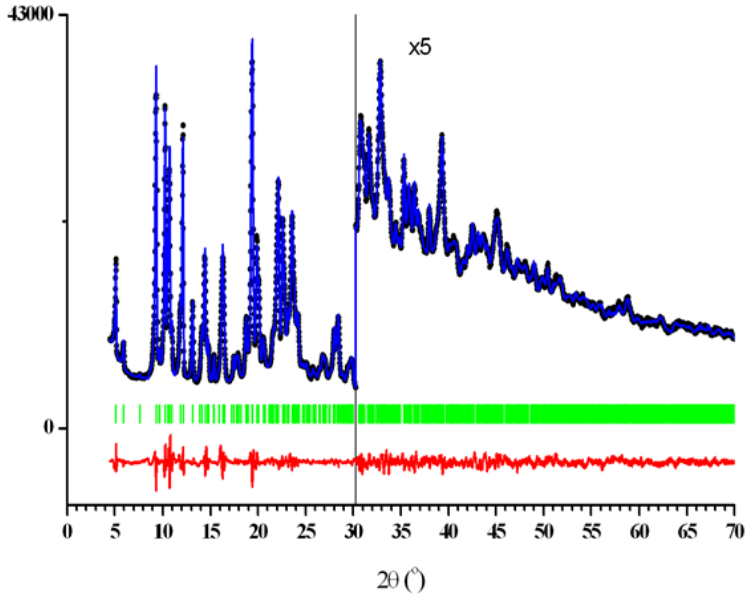


Figure S8. The Rietveld plot for **IPCE-1Pd_Im** showing the experimental (black dots), calculated (blue) and difference (red) curves. The vertical green bars denote calculated positions of the diffraction peaks.

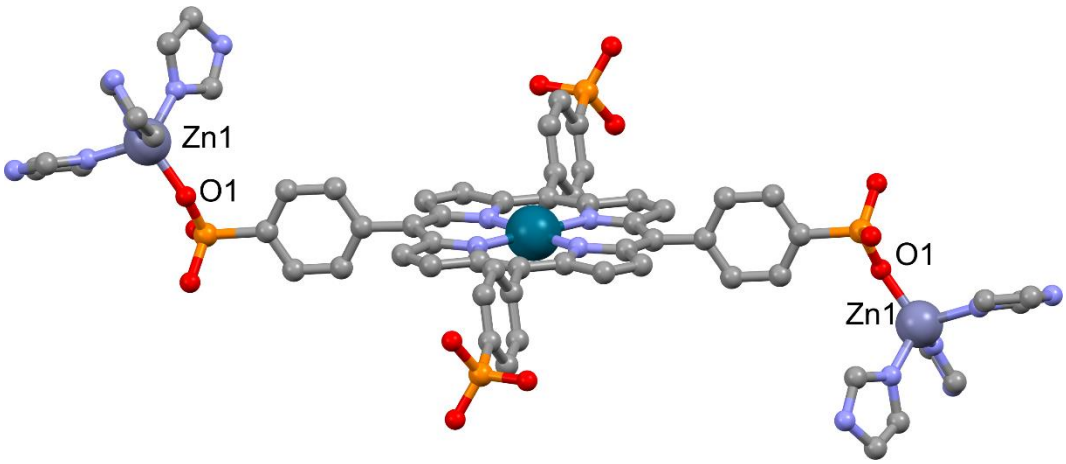


Figure S9. Coordination environment of palladium(II) porphyrinate in **IPCE-1Pd_Im**. Hydrogen atoms are omitted for clarity.

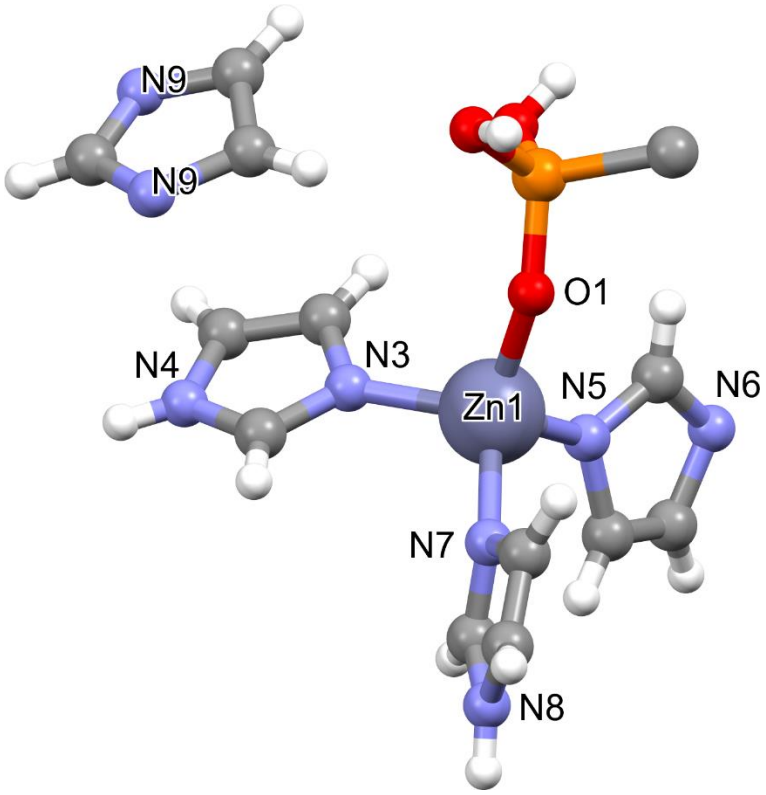


Figure S10. Graphical representation of zinc(II) coordination environment in **IPCE-1Pd_Im**.

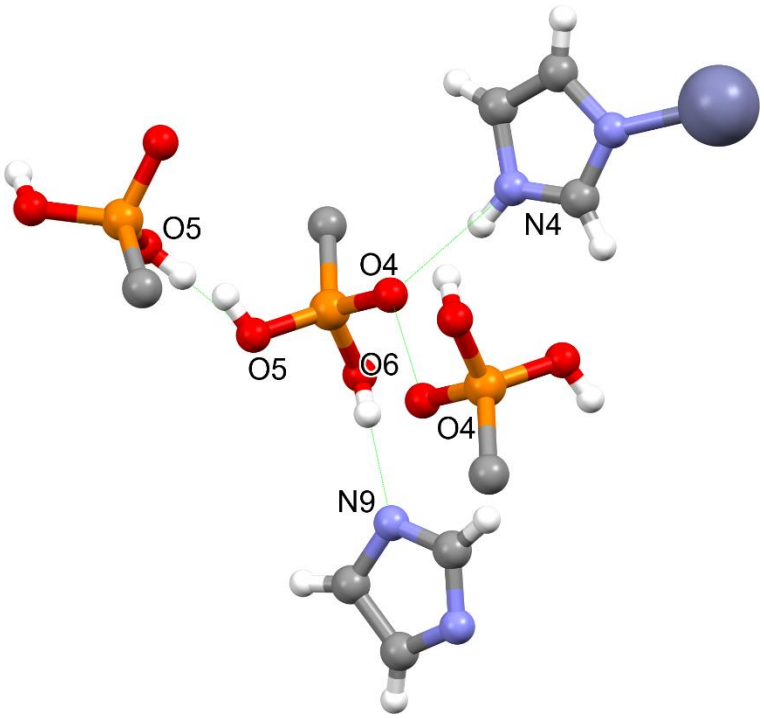


Figure S11. Graphical representation of hydrogen bonds of coordinatively free phosphonate groups of Pd-H_7TPPP$^-$ in **IPCE-1Pd_Im**.

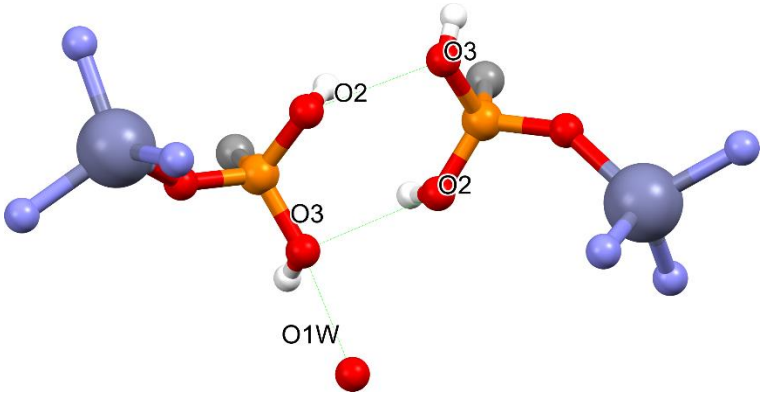


Figure S12. Graphical representation of hydrogen bonds of coordinated phosphonate groups of Pd-H_7TPPP$^-$ in **IPCE-1Pd_Im**.

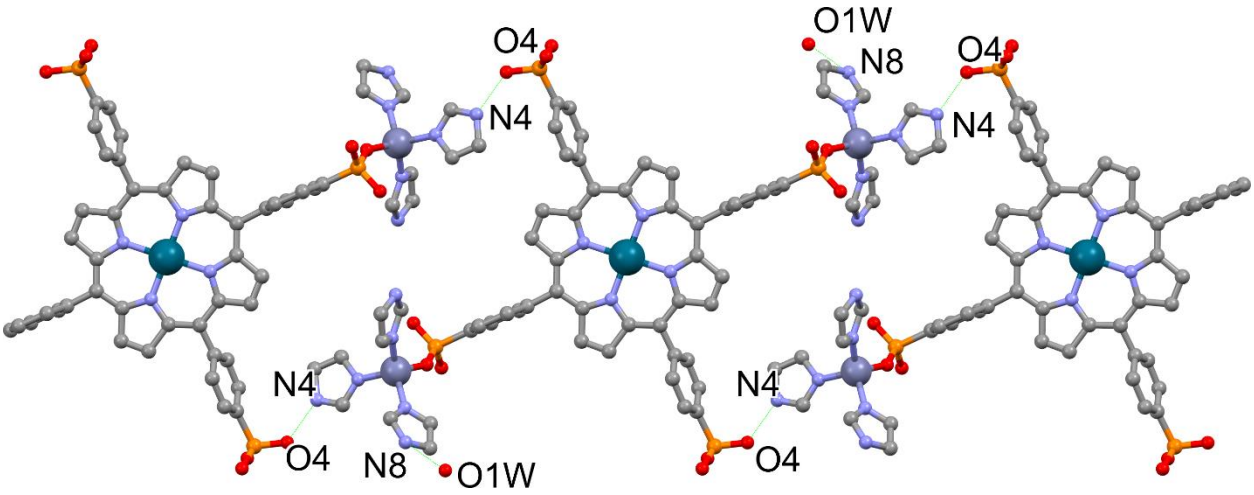
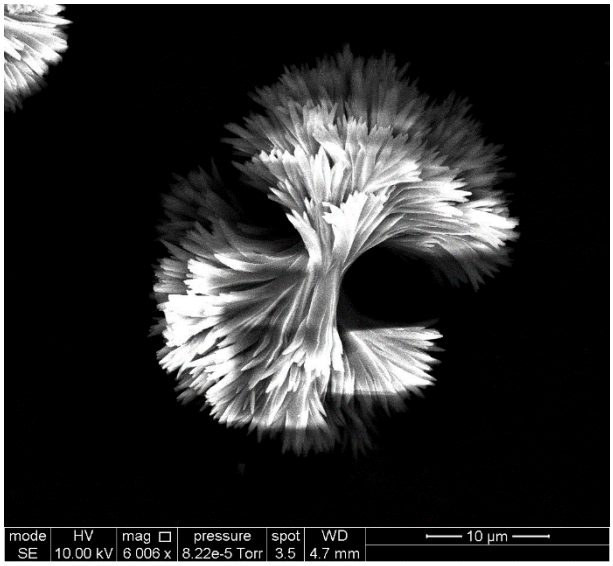
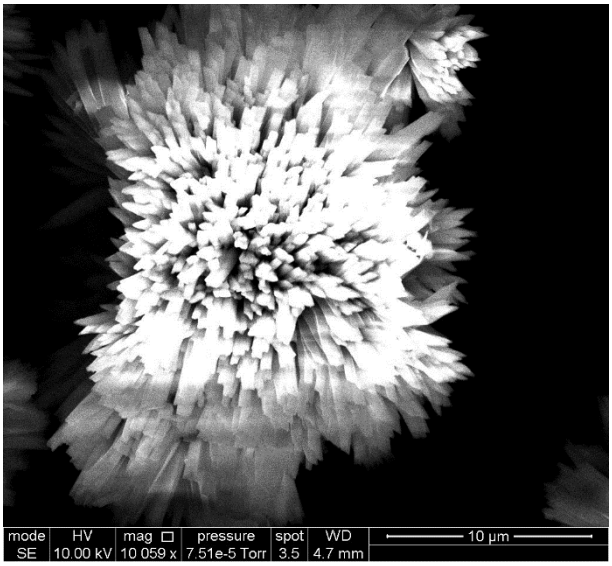


Figure S13. Graphical representation of hydrogen bonds of coordinated imidazole molecules in **IPCE-1Pd_Im**.

SEM and EDX data of IPCE-1Pd





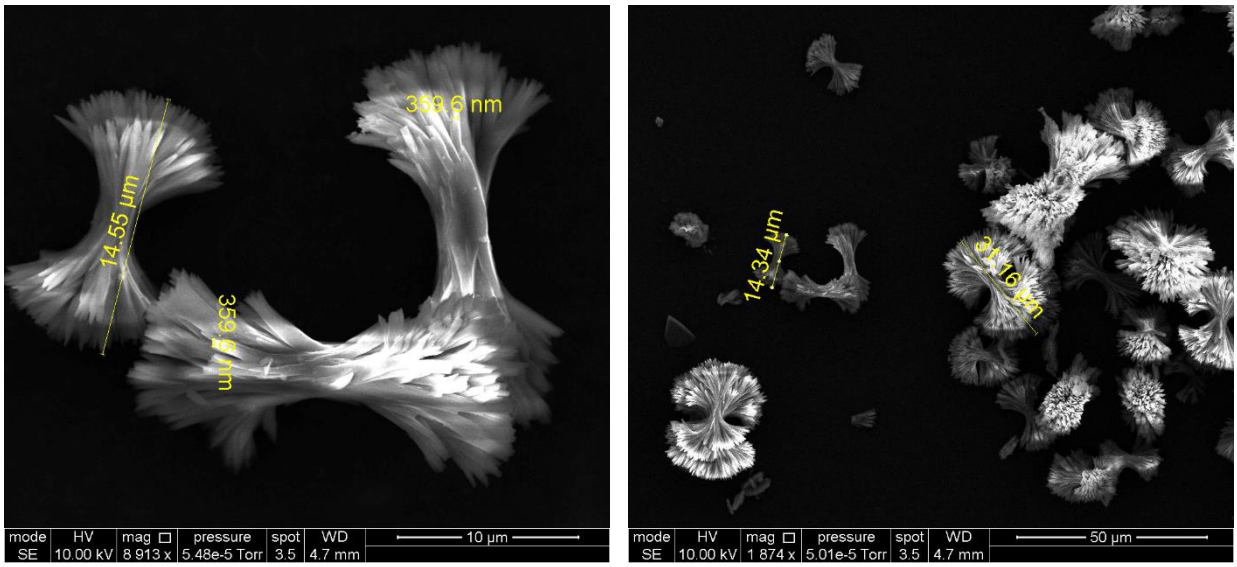


Figure S14. SEM images of dried sample of **IPCE-1Pd**.

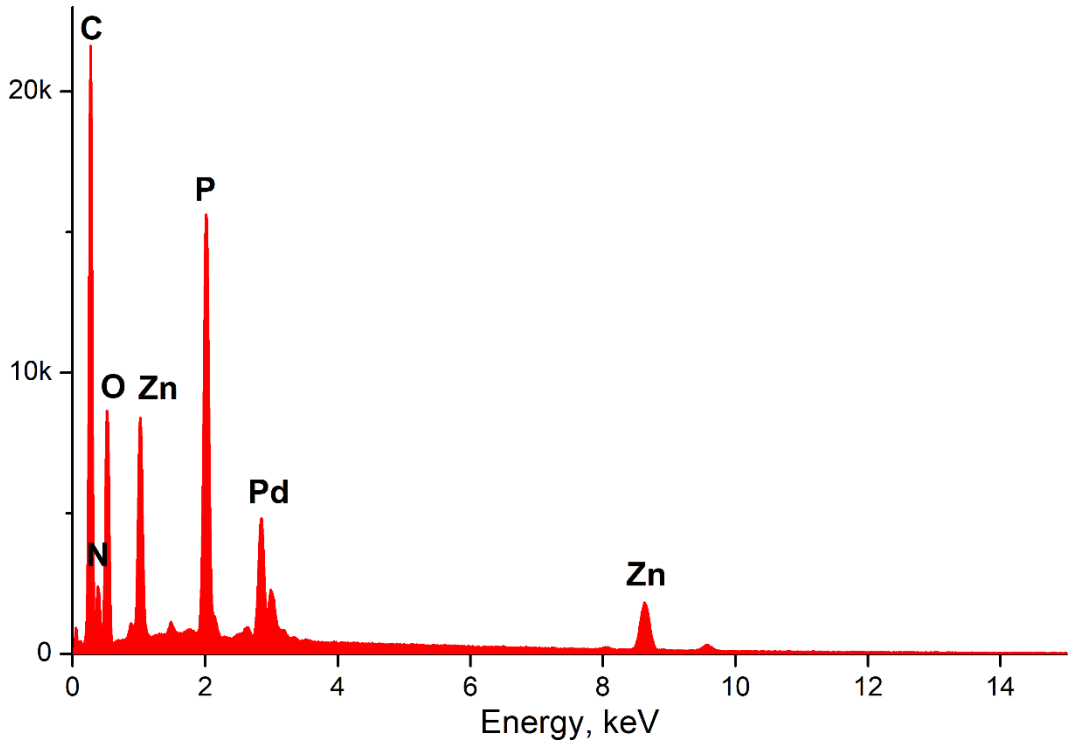


Figure S15. EDX spectrum of **IPCE-1Pd**.

Table S9. Elemental analysis of **IPCE-1Pd** based on EDS spectroscopy data.

Element	C	N	O	P	Pd	Zn
Wt, %	50.70	09.82	21.23	06.09	05.35	06.81
At, %	63.96	10.62	20.11	02.98	00.76	01.58

XPS data of IPCE-1Pd

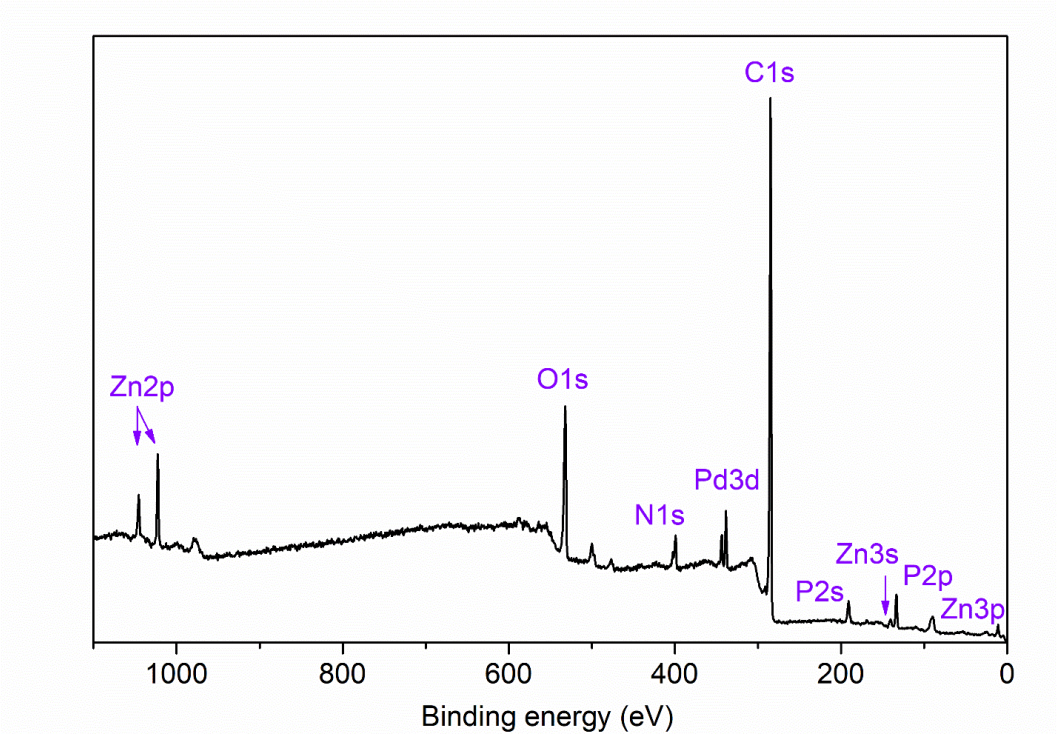


Figure S16. XPS spectrum of **IPCE-1Pd**.

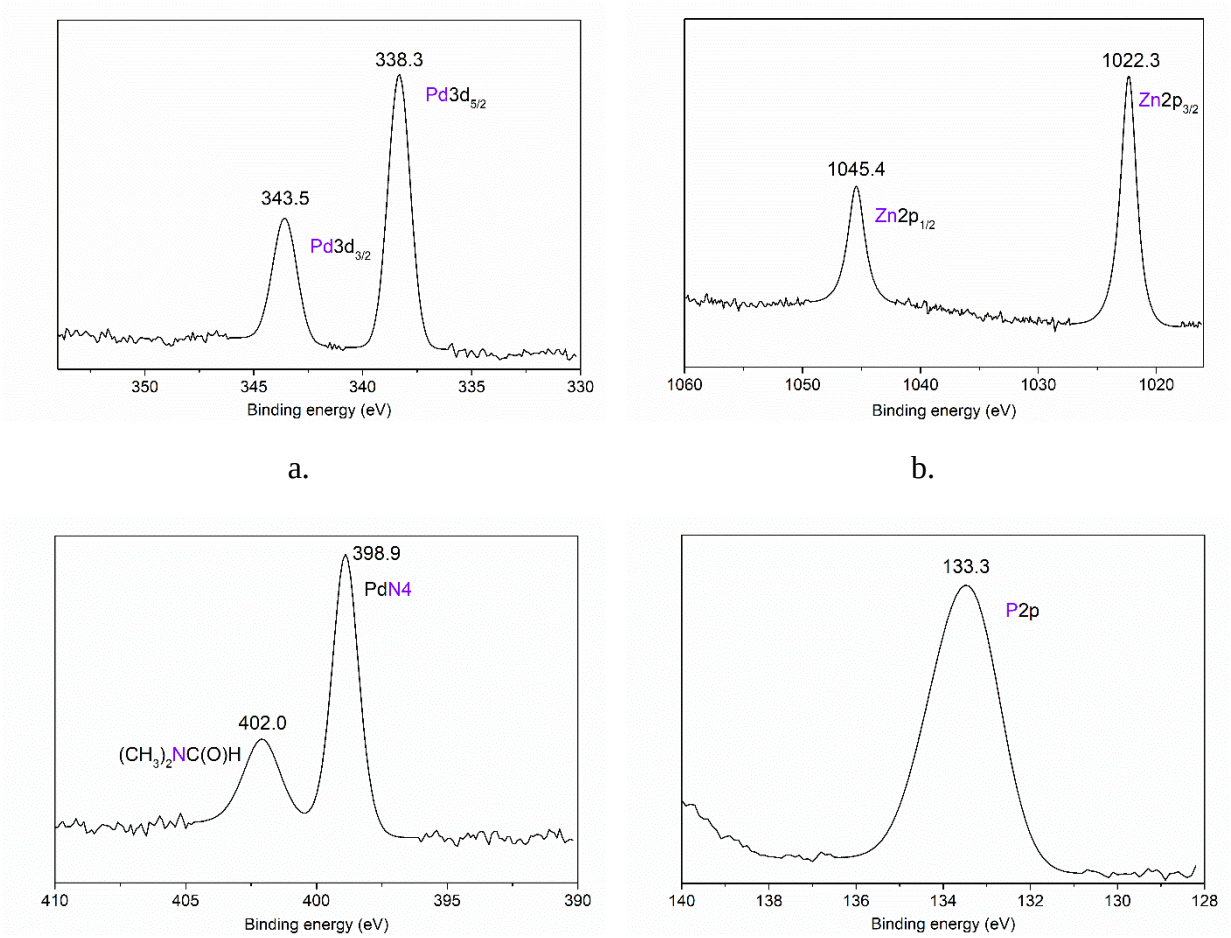


Figure S17. (a) XPS spectrum of Pd3d of **IPCE-1Pd**. (b) XPS spectrum of Zn2p of **IPCE-1Pd**. (c) XPS spectrum of N1s of **IPCE-1Pd**. (d) XPS spectrum of P2p of **IPCE-1Pd**.

Thermal investigations of IPCE-1Pd

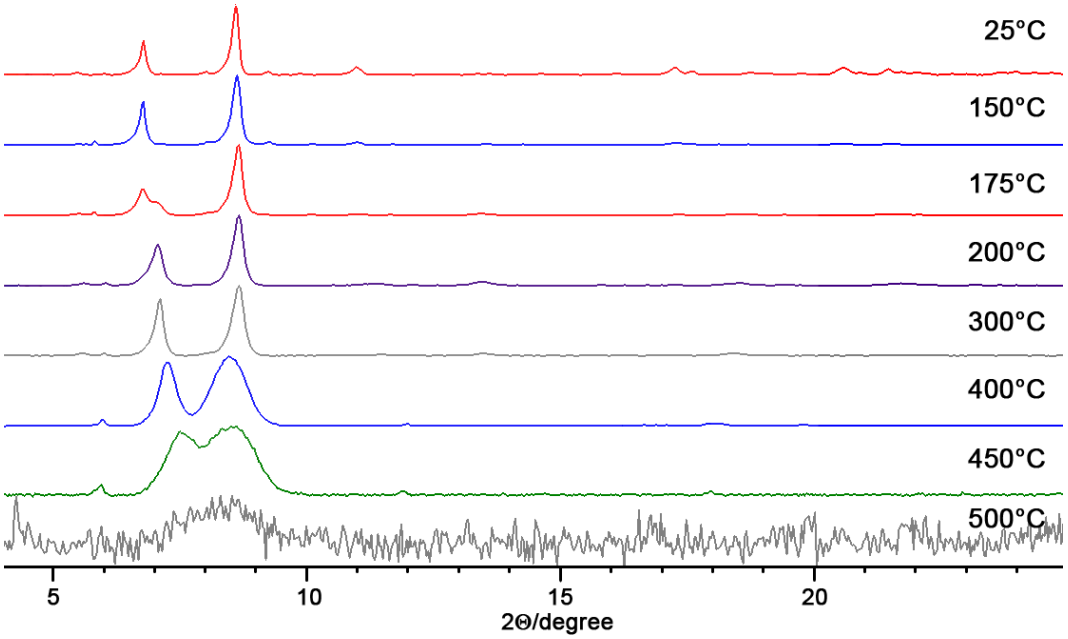


Figure S18. VT-PXRD patterns of **IPCE-1Pd** in the range of 25-500 °C.

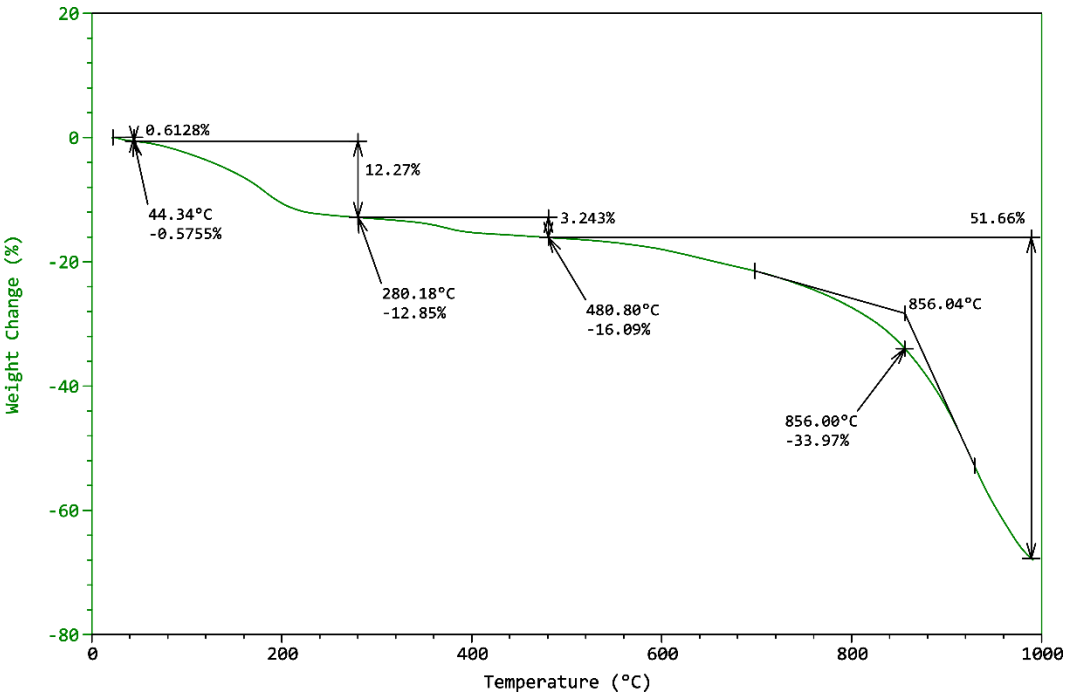


Figure S19. The TGA plot of **IPCE-1Pd**.

Chemical stability of IPCE-1Pd

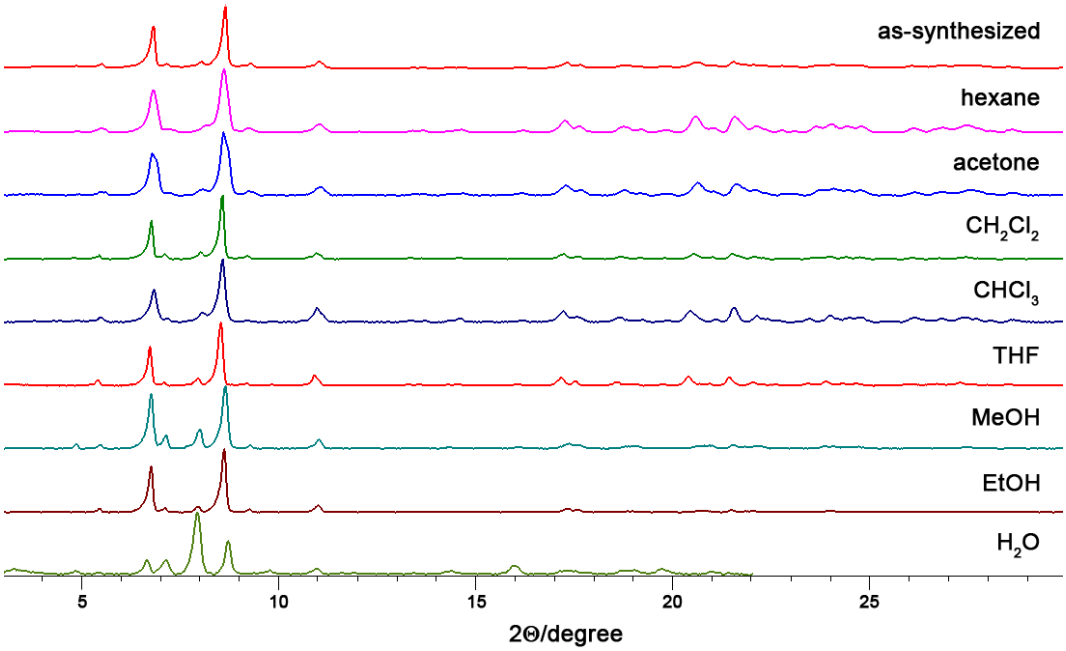


Figure S20. PXRD patterns of **IPCE-1Pd** treated by immersion in different solvents for 7 days.

EDX data of IPCE-1Pd_Im

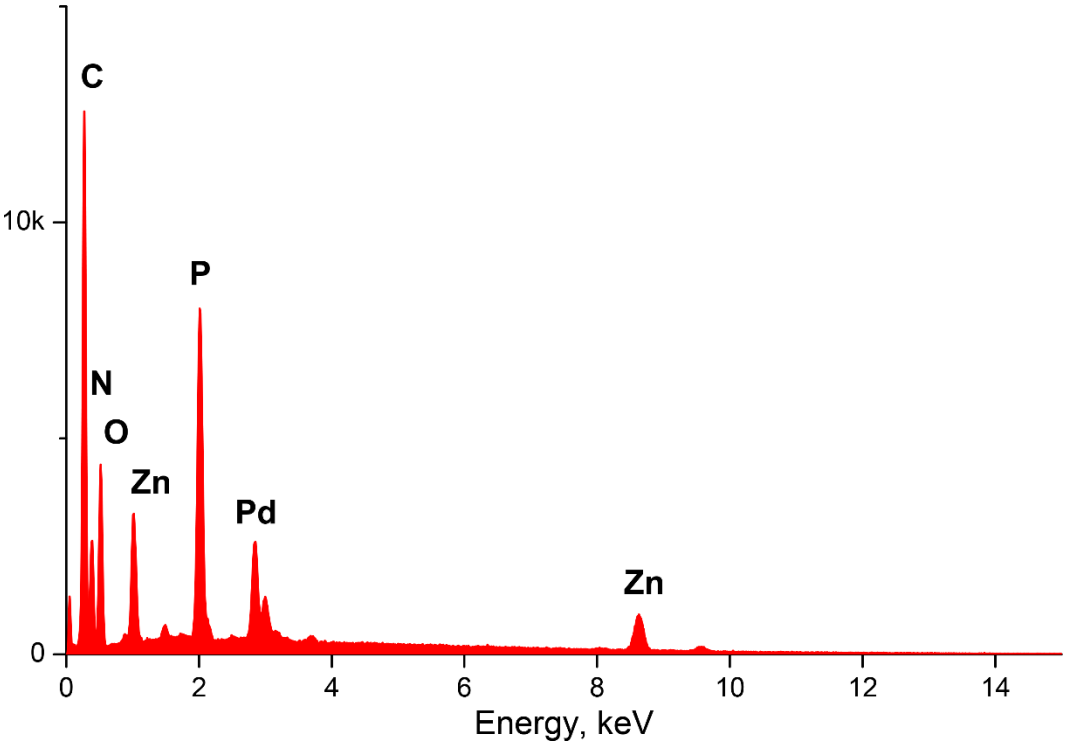


Figure S21. EDX spectrum of **IPCE-1Pd_Im**.

Table S10. Elemental analysis of **IPCE-1Pd_Im** based on EDS spectroscopy data.

Element	C	N	O	P	Pd	Zn
Wt, %	46.26	17.99	18.26	05.56	05.47	06.46
At, %	58.30	19.44	17.27	02.72	0.78	01.50

Thermal investigations of IPCE-1Pd_Im

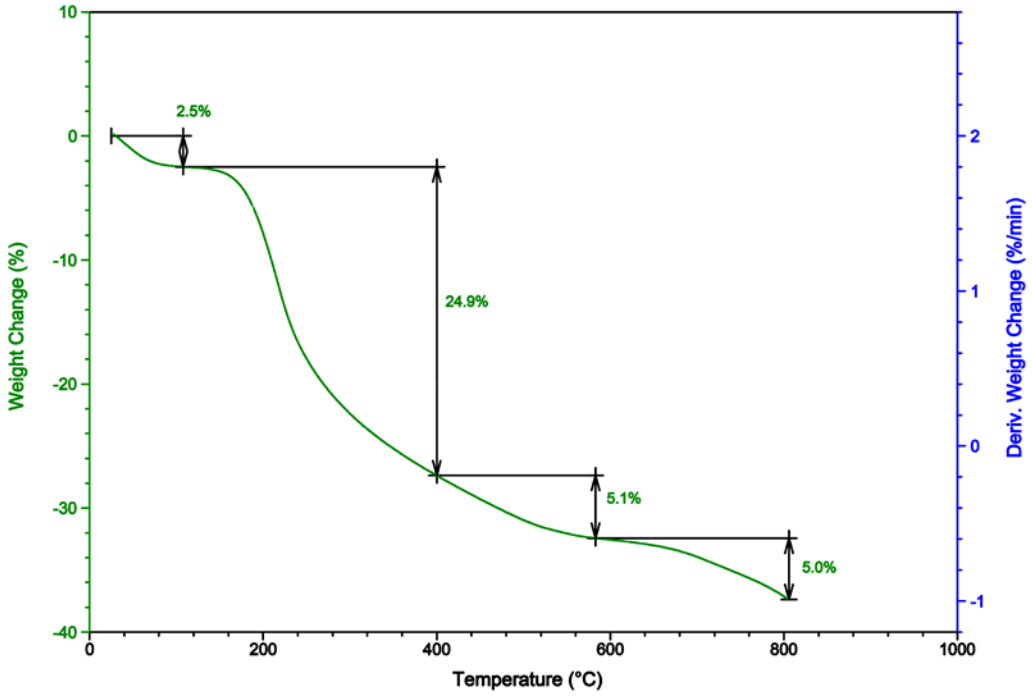


Figure S22. The TGA plot of **IPCE-1Pd_Im.**

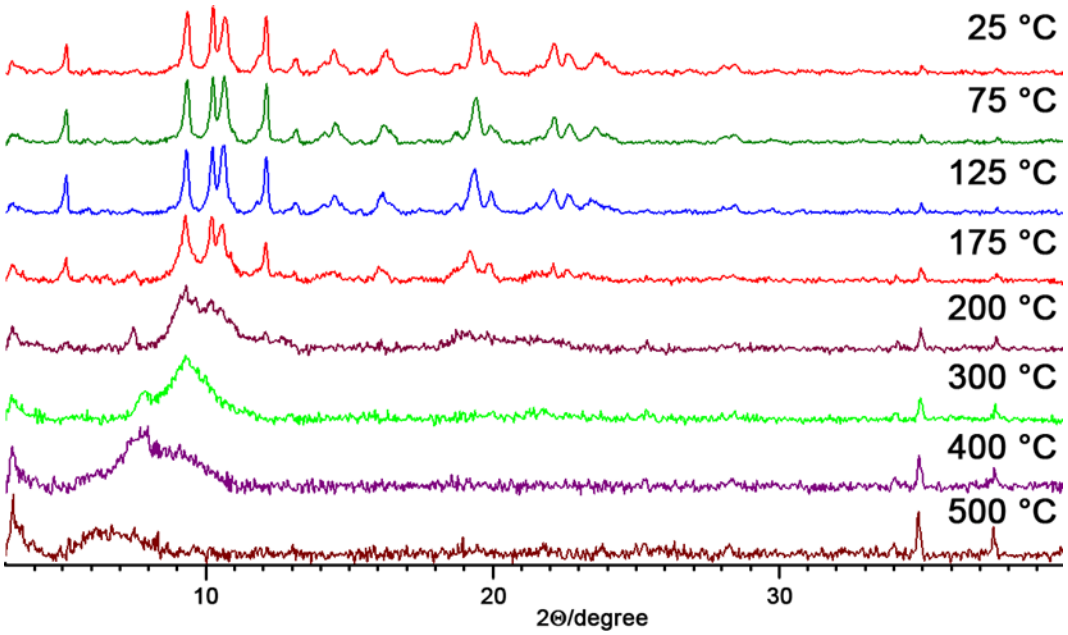
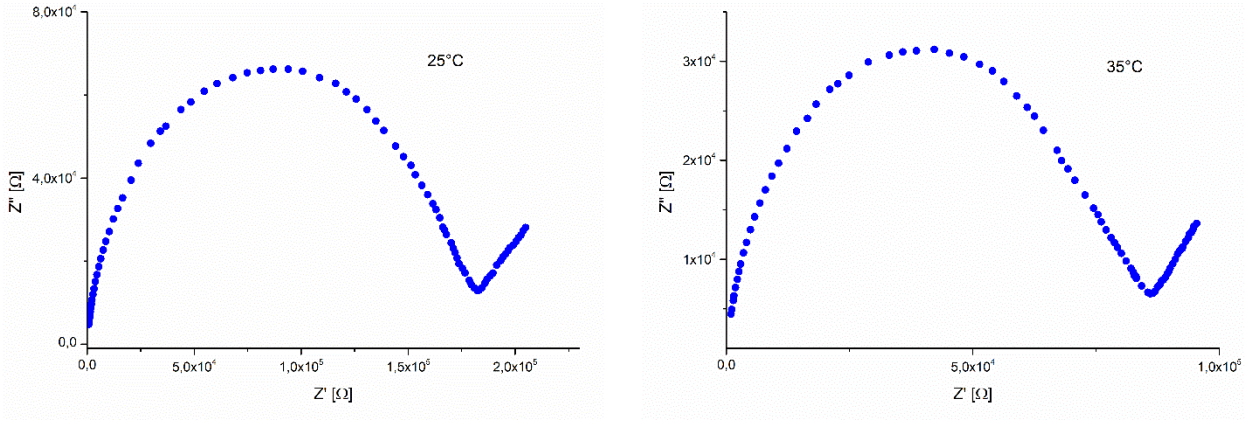


Figure S23. VT-PXRD patterns of **IPCE-1Pd_Im** in the range of 25-500 °C.

Proton conductivity of IPCE-1Pd and IPCE-1Pd_Im



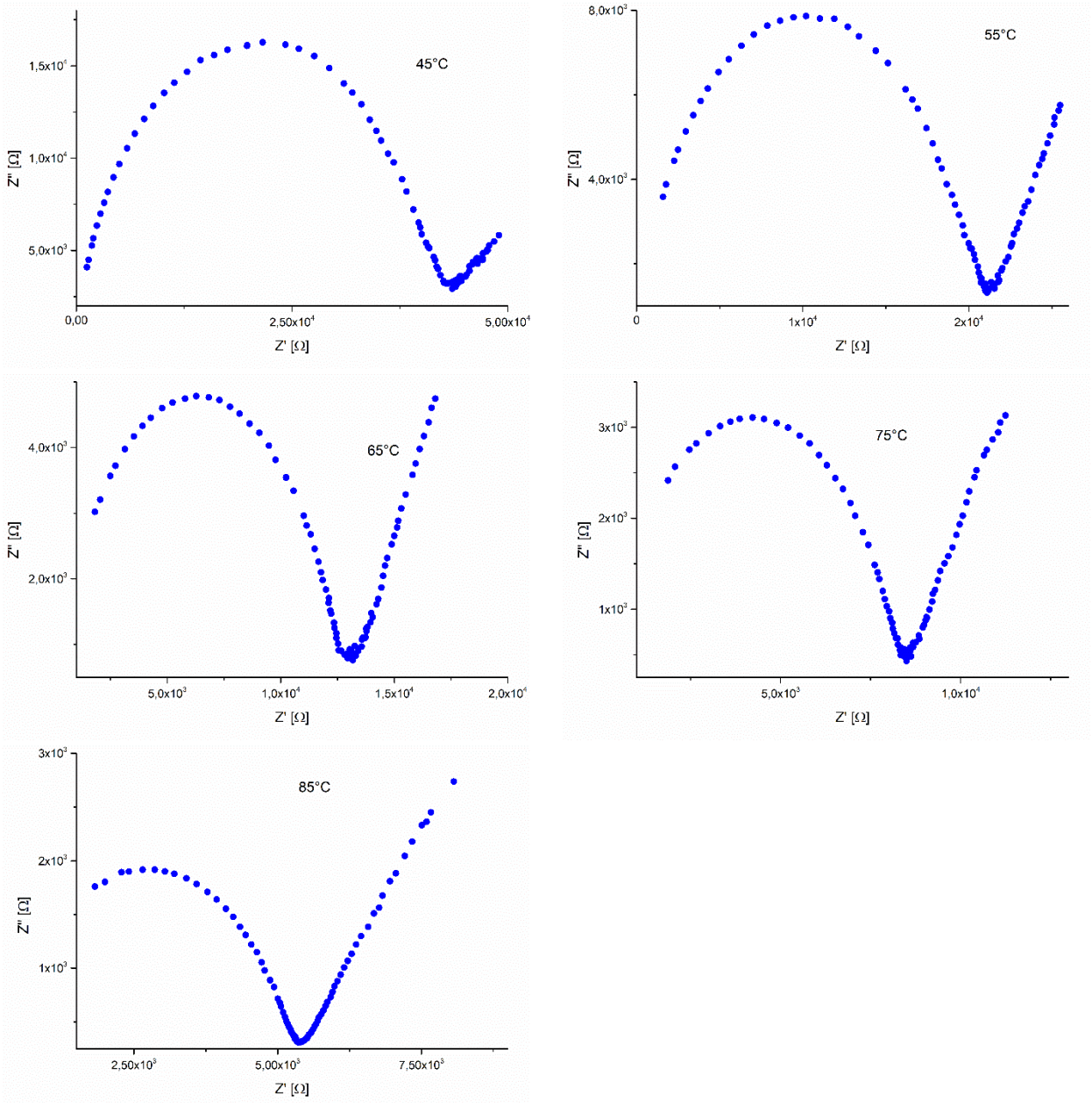
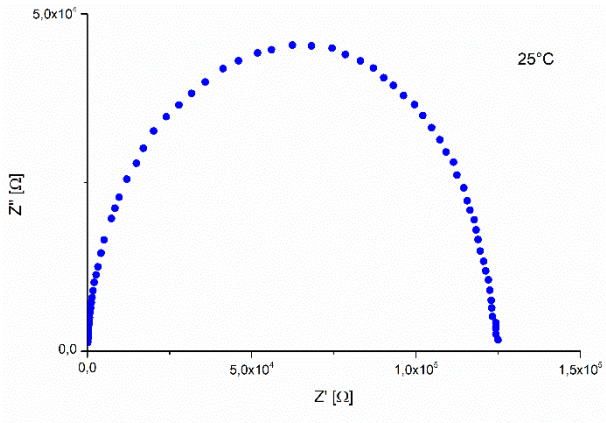
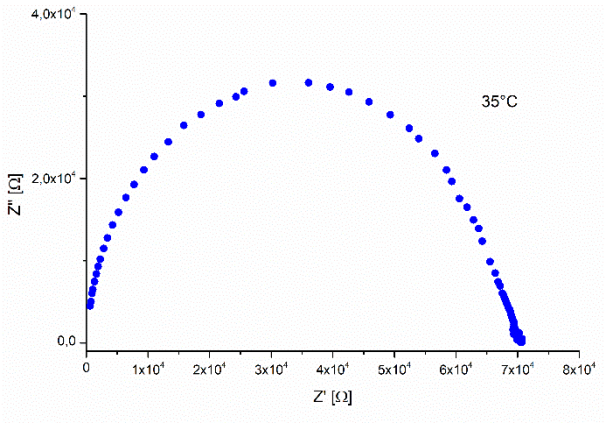
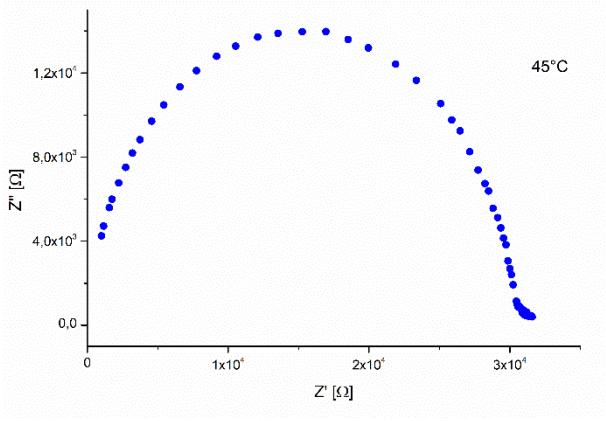
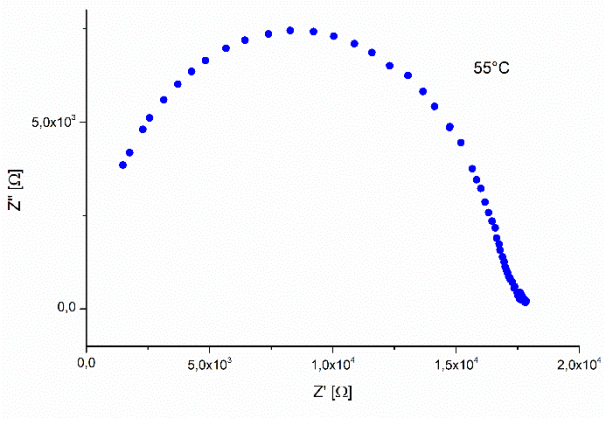


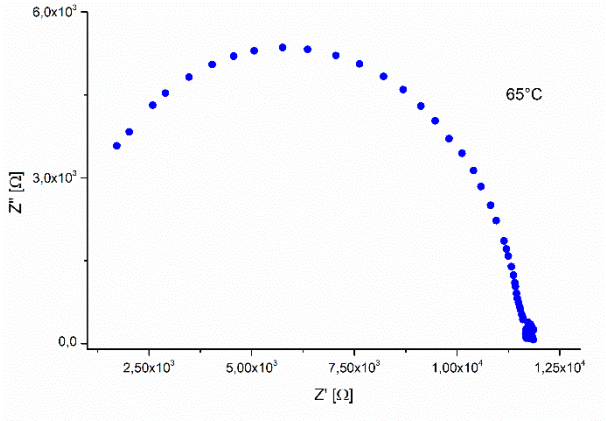
Figure S24. Nyquist plots of **IPCE-1Pd** at 85% RH and different temperatures.

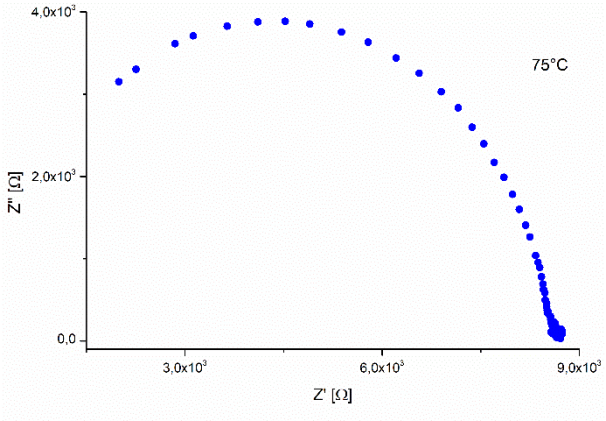

25°C
Z'' [Ω]
Z' [Ω]
0,0
5,0x10^4
1,0x10^5
1,5x10^5


35°C
Z'' [Ω]
Z' [Ω]
0,0
2,0x10^4
0
1x10^4
2x10^4
3x10^4
4x10^4
5x10^4
6x10^4
7x10^4
8x10^4


45°C
Z'' [Ω]
Z' [Ω]
0,0
4,0x10^3
8,0x10^3
0
1x10^4
2x10^4
3x10^4


55°C
Z'' [Ω]
Z' [Ω]
0,0
5,0x10^3
1,0x10^4
1,5x10^4
2,0x10^4


65°C
Z'' [Ω]
Z' [Ω]
0,0
3,0x10^3
2,50x10^3
5,00x10^3
7,50x10^3
1,00x10^4
1,25x10^4


75°C
Z'' [Ω]
Z' [Ω]
0,0
2,0x10^3
3,0x10^3
6,0x10^3
9,0x10^3

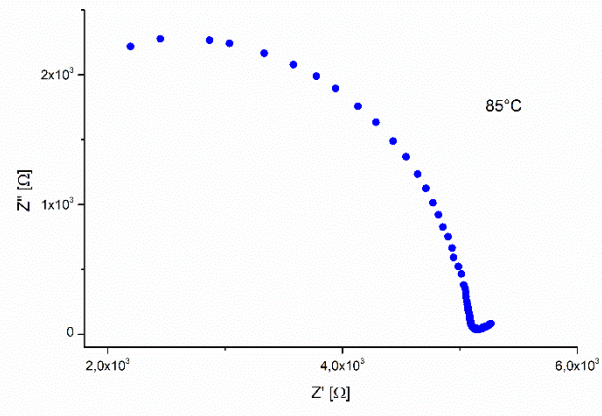


Figure S25. Nyquist plots of **IPCE-1Pd_Im** at 85% RH and different temperatures.

Crystal packings of IPCE-1Pd and IPCE-1Pd_Im

IPCE-1Pd.

The coordinating Zn-O bonds link the molecules into 3D MOF with channels extending along the *b* axis (**Figure S26**). These channels are filled with *dmf* and H_2O molecules which interact with rigid 3D framework *via* O-H…O hydrogen bonds (**Table S4**, **Figure S27**).

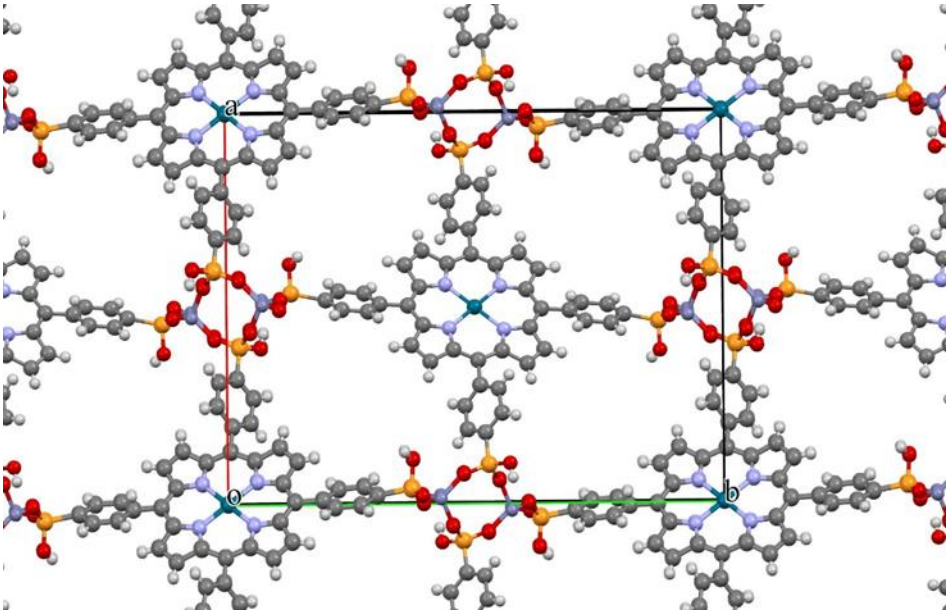


Figure S26. A portion of the crystal packing of **IPCE-1Pd** viewed along the c axis. The *dmf* and H_2O molecules are not drawn to clearly show the empty channels.

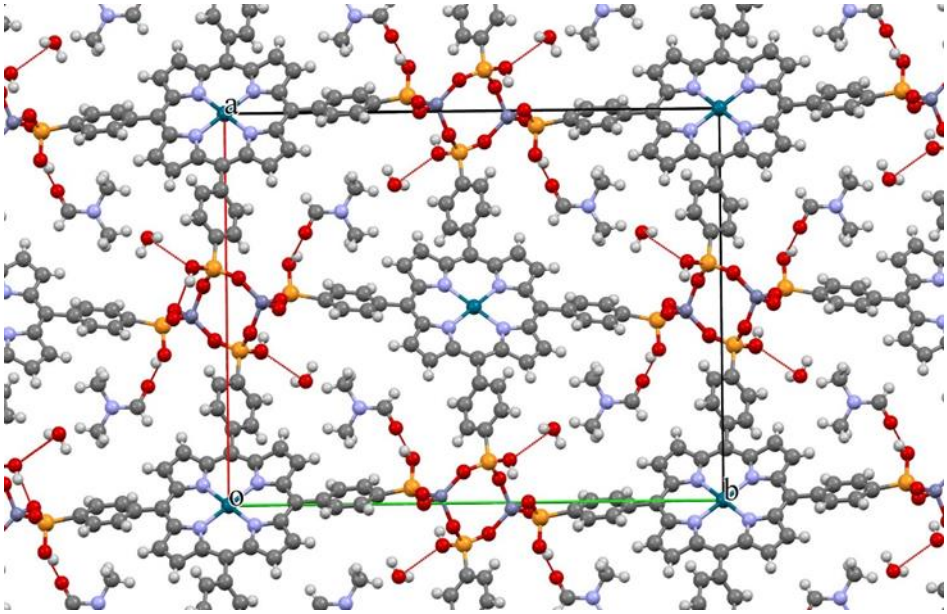


Figure S27. A portion of the crystal packing of **IPCE-1Pd** viewed along the *c* axis and showing the *dmf* and H_2O molecules in the channels. Thin red lines denote intermolecular O-H…O hydrogen bonds.

IPCE-1Pd_Im.

To clearly show the formation of 3D HOF by the strong hydrogen bonds (with O,N…H distance < 2.05 Å) we exclude the disordered imidazole (N10/N11/C34-C36) and two water molecules (O1w, O2w), which are situated in the voids, from further consideration. In the crystal, the O6-H6…N9 hydrogen bond (Table S8) link the Pd-H_7TPPP cations and imidazolate anions into 1D chains running in [102] direction (**Figure S28**). The N4-H4A…O4 hydrogen bond (Table S8) link the cations into the chains extending in [122] direction (**Figure S29**). A combination of two aforementioned hydrogen-bonds leads to formation of thick 2D layers (**Figure S30**). Finally, the O5-H5A-O5* hydrogen bonds contribute to consolidation of 3D HOF structure.

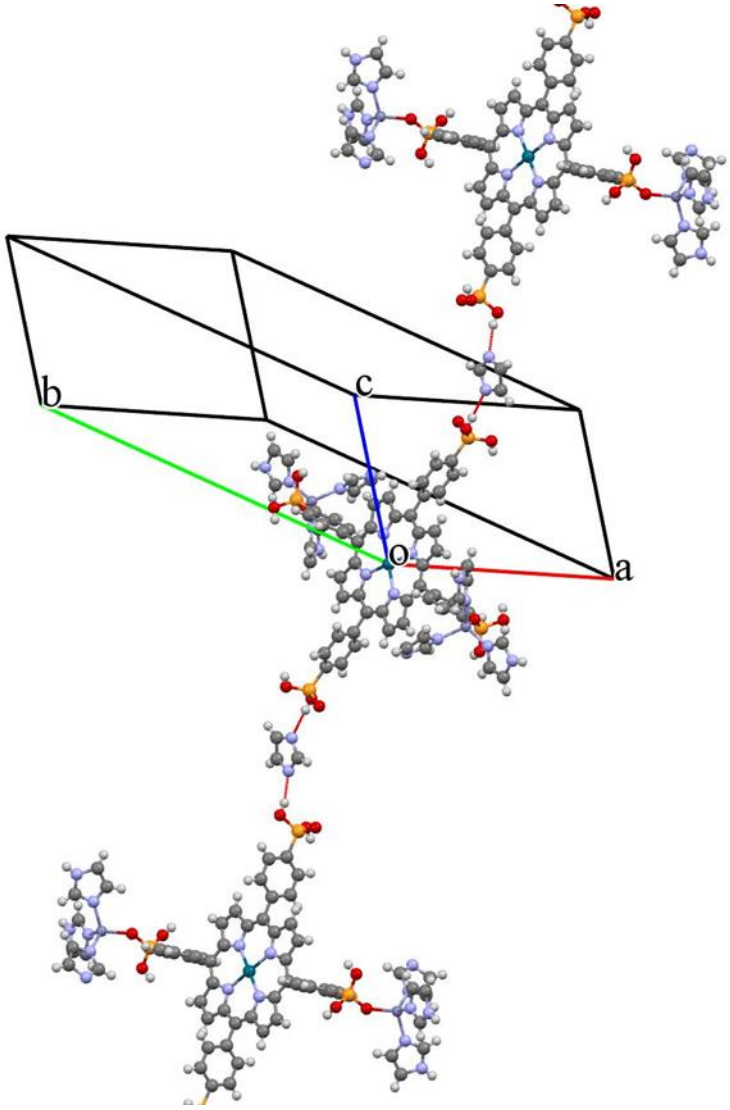


Figure S28. A hydrogen-bonded chain in **IPCE-1Pd_Im** running in [102] direction. Thin red lines denote intermolecular O-H…N hydrogen bonds.

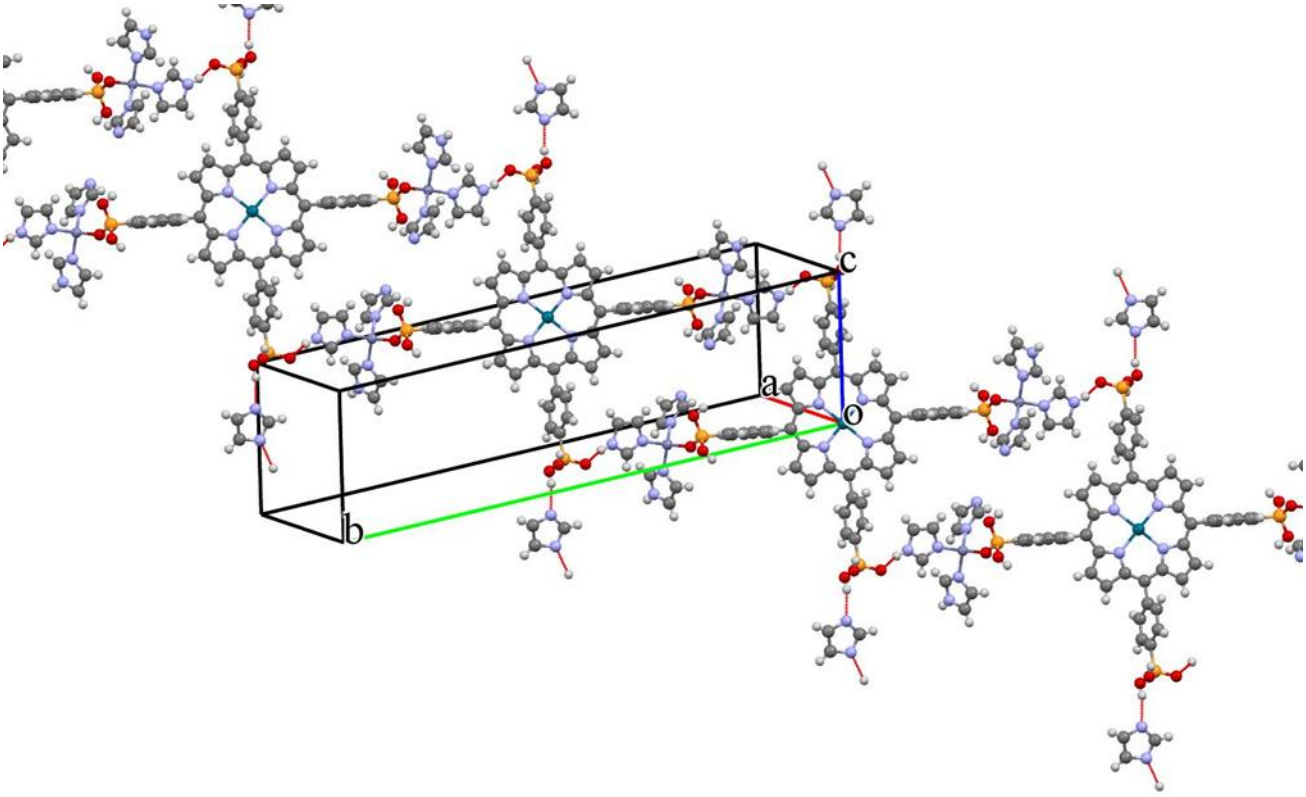


Figure S29. A schematic representation of the hydrogen-bonded chain of the cations in **IPCE-1Pd_Im** extended in [122] direction. Thin red lines denote intermolecular N-H…O and O-H…N hydrogen bonds.

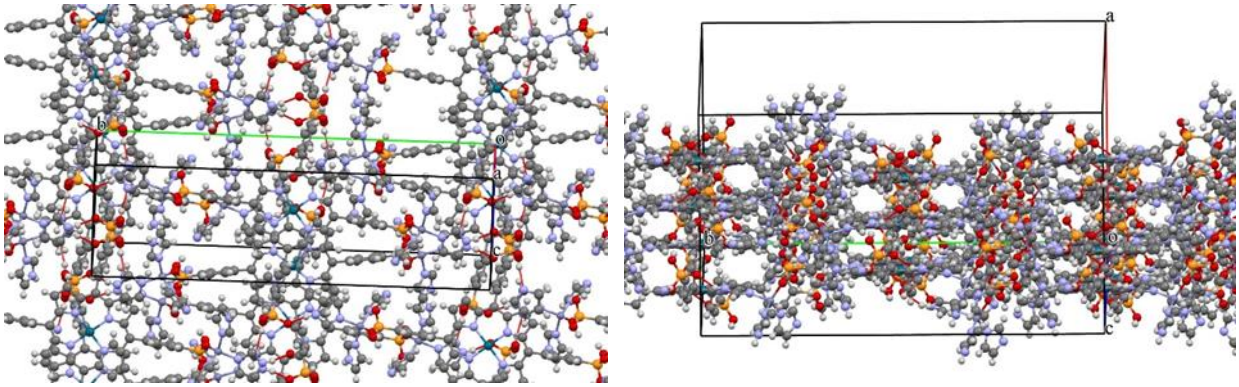


Figure S30. View of the hydrogen-bonded 2D layer in **IPCE-1Pd_Im** in two orthogonal directions.

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