Electronic Supporting Information

An Anionic Porphyrinylphosphonate-Based Hydrogen-Bonded Organic Framework: Optimization of the Proton Conductivity through the Exchange of Counterions

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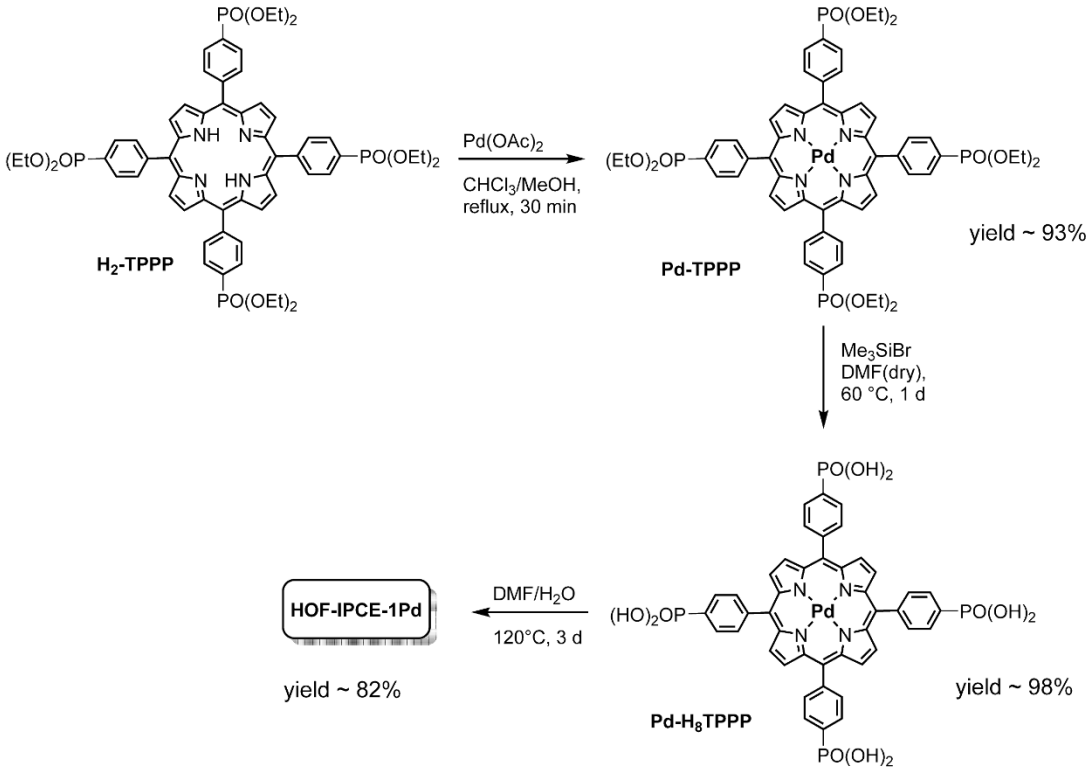
Synthesis of HOF-IPCE-1Pd



Scheme S1. Synthetic route towards **HOF-IPCE-1Pd**.

Spectral characterization of compounds

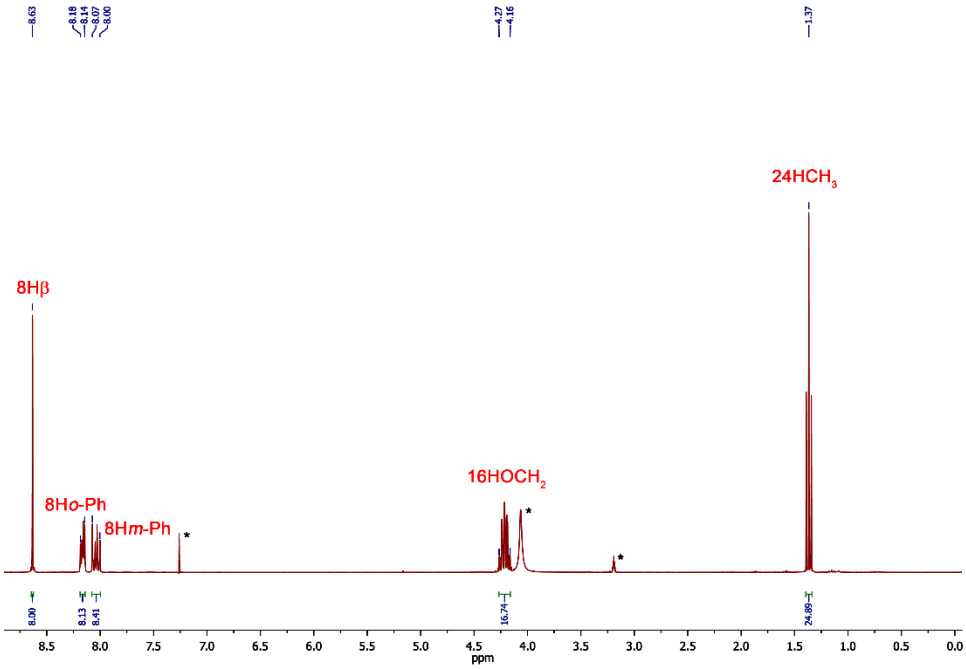


Figure S1. ^{1}H NMR spectrum of **Pd-TPPP** ($CDCl_3$/MeOD 2:1, v/v). Solvent peaks are indicated with *(δ_H 7.26 ppm – $CHCl_3$, 4.06 ppm – DOH and H_2O, 3.19 ppm – CHD_2OD).

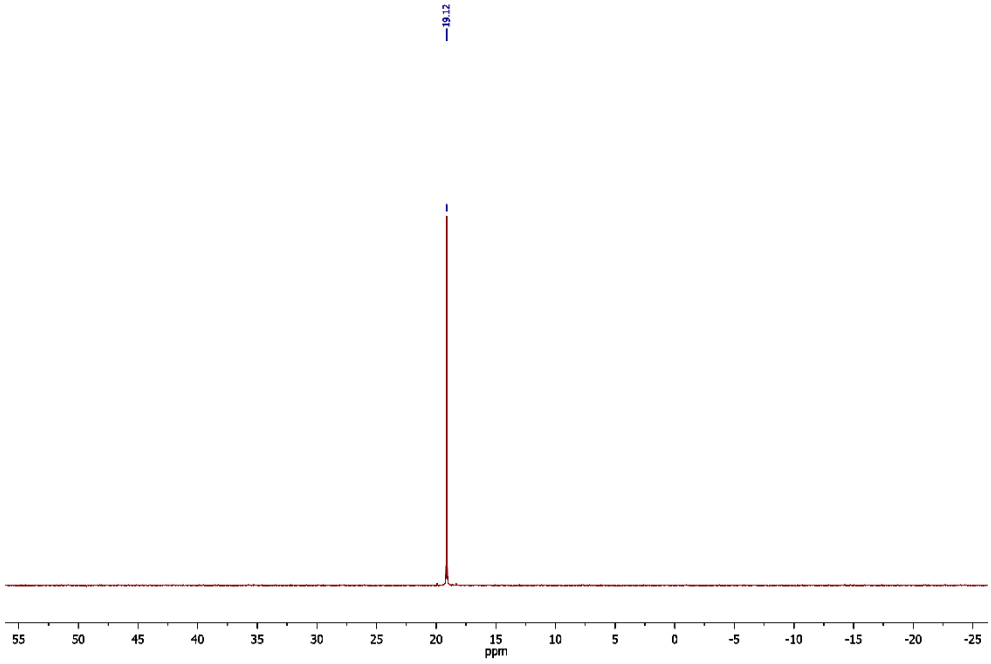


Figure S2. ^{31}P{^{1}H} NMR spectrum of **Pd-TPPP** ($CDCl_3$/MeOD 2:1, v/v).

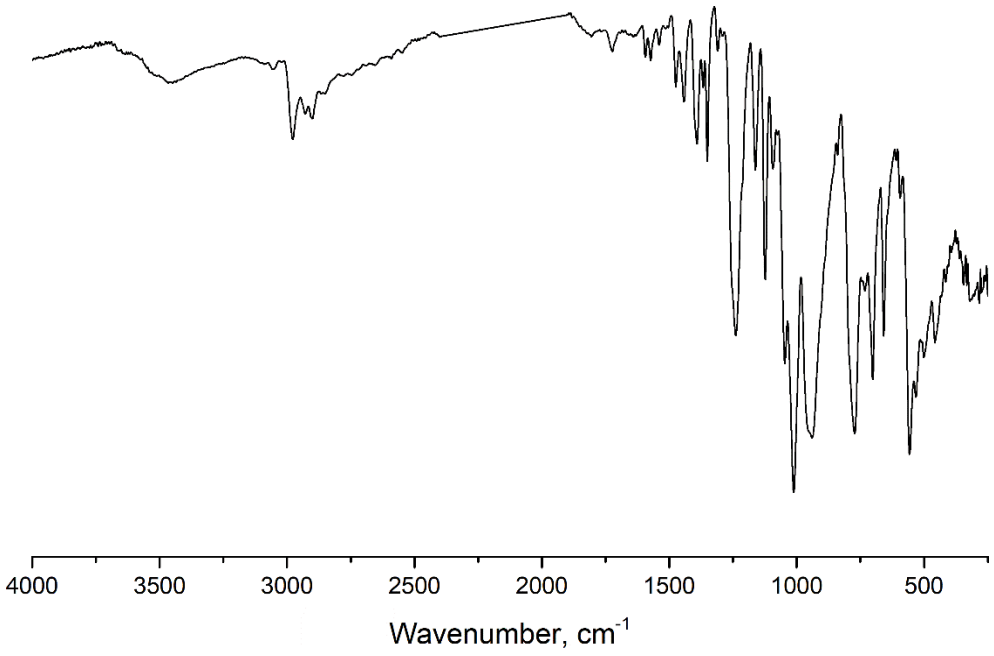


Figure S3. IR spectrum of **Pd-TPPP**.

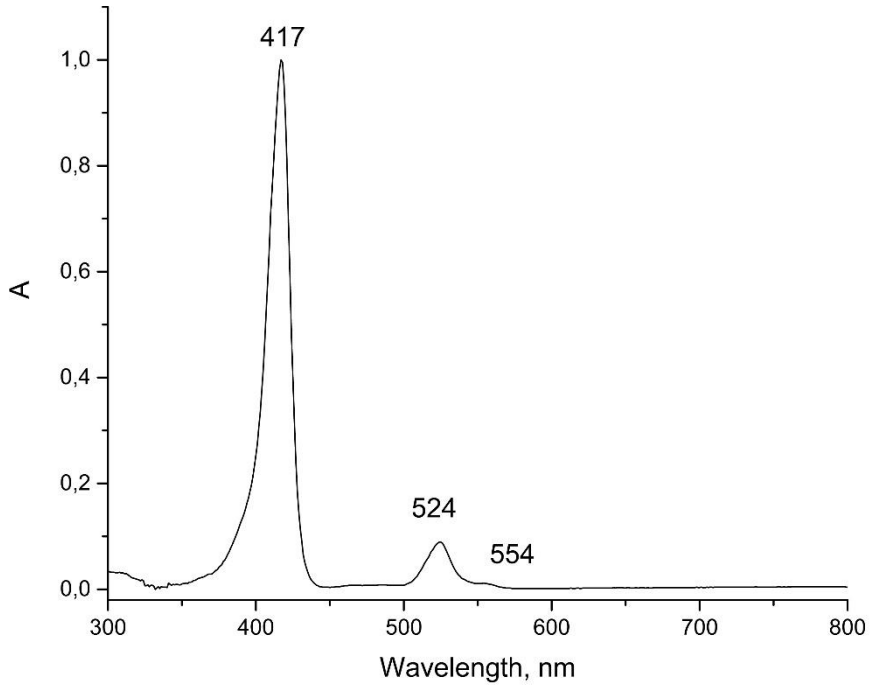


Figure S4. Normalized UV-vis spectrum of **Pd-TPPP** in CH_2Cl_2 (c = 7.9 μM).

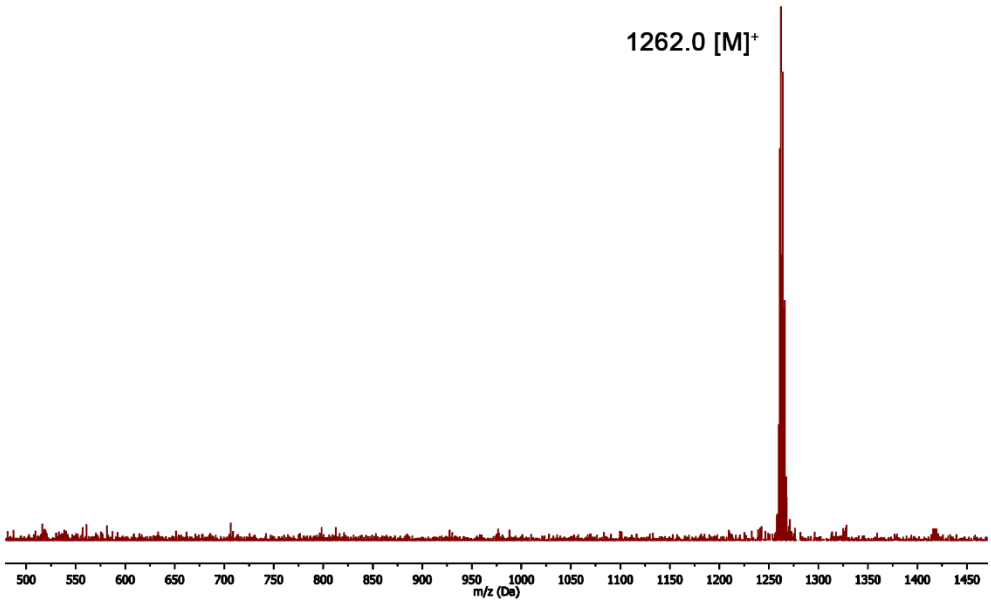


Figure S5. MALDI TOF mass-spectrum of **Pd-TPPP**.

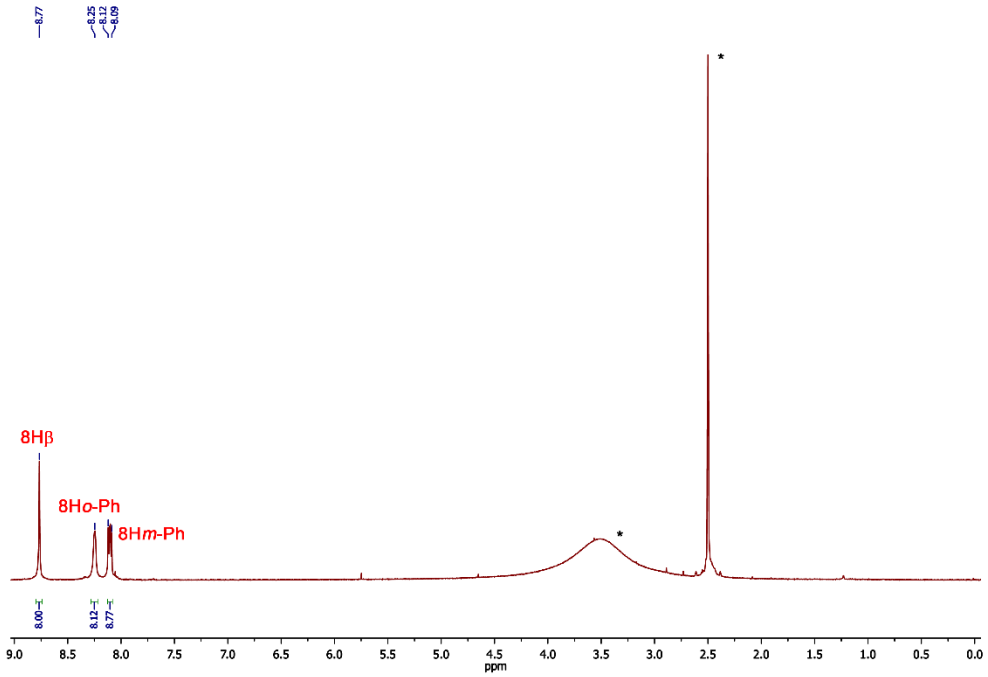


Figure S6. ^{1}H NMR spectrum of **Pd-H$_8$TPPP** (DMSO-*d6*) at 333 K. Solvent peaks are indicated with *(δ_H 3.52 ppm – DOH and H_2O, 2.50 ppm – $(CD_3)SO(CD_2H)$).

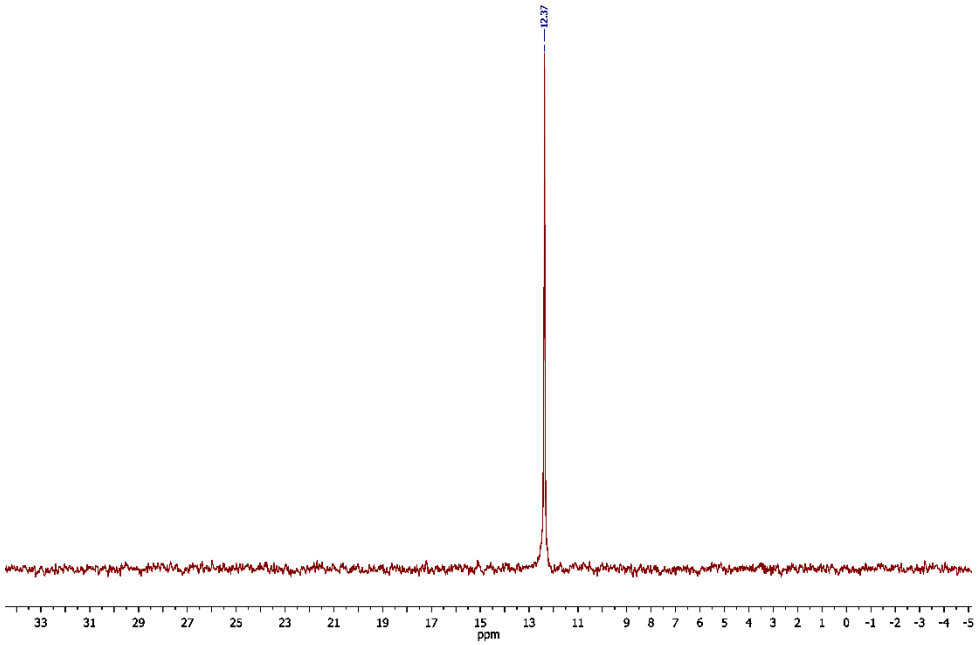


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **Pd-H$_8$TPPP** (DMSO-*d6*) at 333 K.

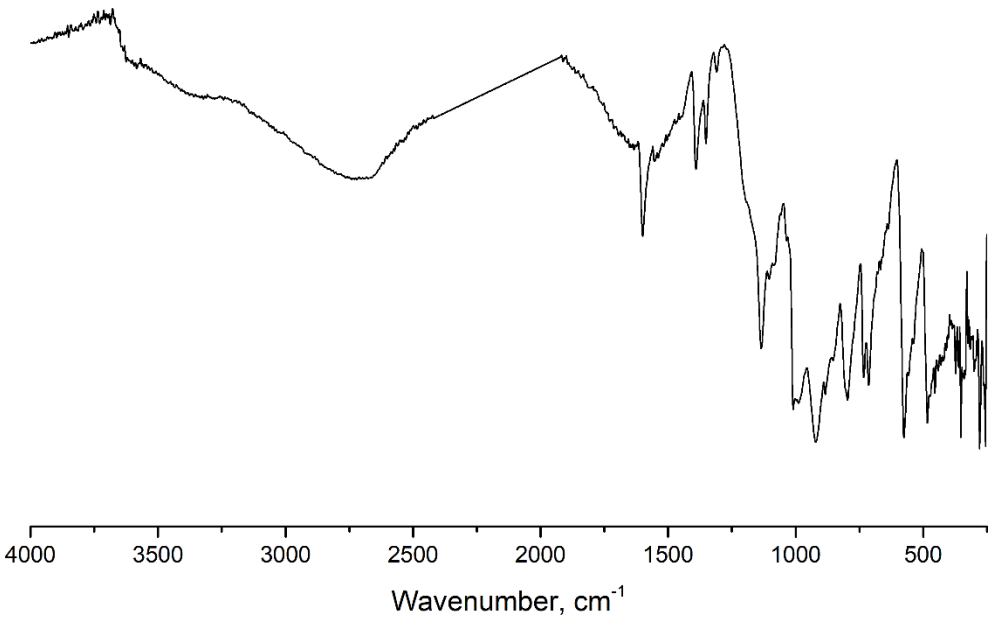


Figure S8. IR spectrum of **Pd-H$_8$TPPP**.

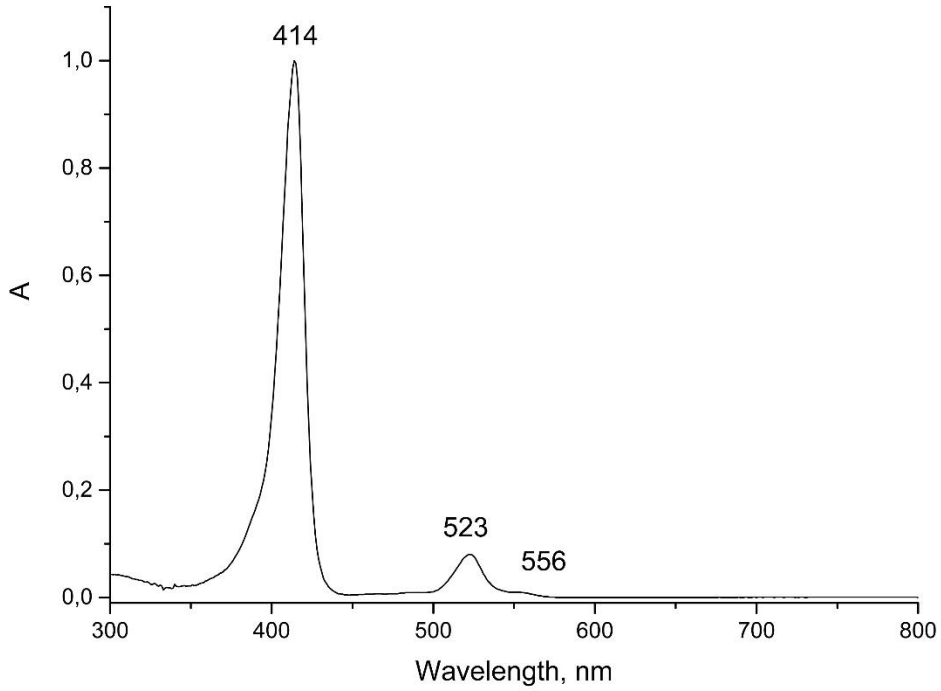


Figure S9. UV-vis absorption spectrum of **Pd-H$_8$TPPP** in H_2O + 50 μL of saturated solution of NaOH in H_2O (c = 8.65 μM).

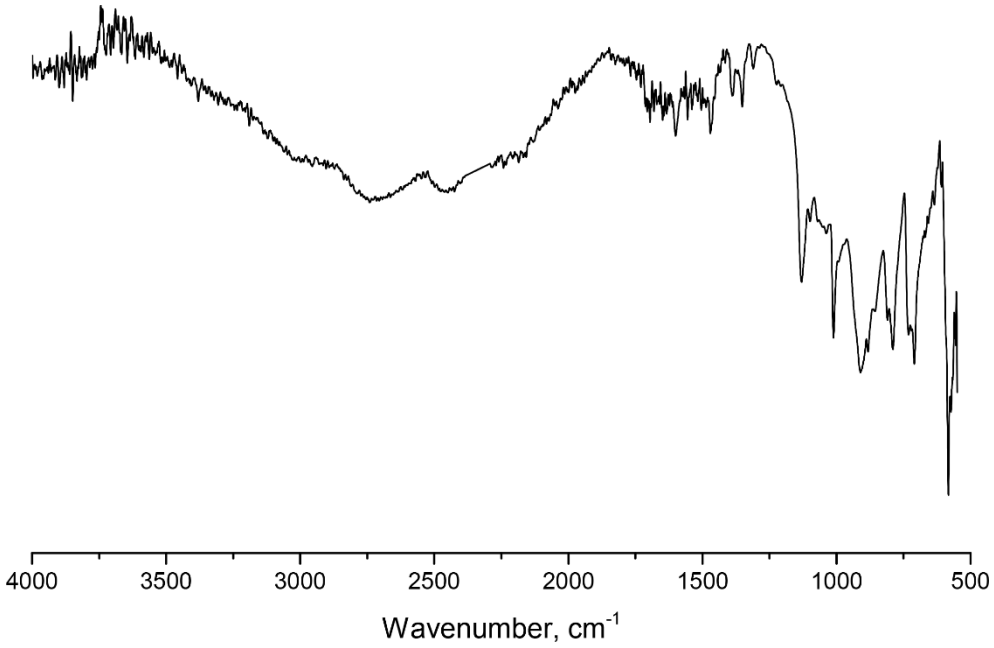


Figure S10. IR spectrum of **HOF-IPCE-1Pd**.

Structural characterization of HOF-IPCE-1Pd

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

Identification code	**HOF-IPCE-1Pd**
CCDC number	2151260
Chemical formula moiety	$C_{44}H_{29}N_4O_{12}P_4Pd$, 3($C_2H_8N$), C_3H_7NO
Empirical formula	$C_{53}H_{60}N_8O_{13}P_4Pd$
Formula weight	1247.37
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	13.0985(7)
b/Å	13.8588(7)
c/Å	17.8550(9)
α/°	70.315(2)
β/°	82.445(2)
γ/°	78.492(2)
Volume/Å^3	2983.2(3)
Z	2
ρ_{calc}g/cm^3	1.389
μ/mm^{-1}	0.484
F(000)	1288.0
Crystal size/mm^3	0.45 × 0.3 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.156 to 55
Index ranges	$-11 \le h \le 17$, $-18 \le k \le 17$, $-23 \le l \le 23$
Reflections collected	34308
Independent reflections	13510 [R_{int} = 0.0422, R_{sigma} = 0.0609]
Data/restraints/parameters	13510/44/808
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0533, wR_2 = 0.1360
Final R indexes [all data]	R_1 = 0.0766, wR_2 = 0.1501
Largest diff. peak/hole / e Å^{-3}	1.61/-0.93

Table S2. Bond lengths for **HOF-IPCE-1Pd**.

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Pd(01)	N(4)	2.019(3)		C(32)	C(31)	1.442(5)
Pd(01)	N(2)	2.023(3)		C(27)	C(26)	1.393(5)
Pd(01)	N(1)	2.015(3)		C(11)	C(12)	1.435(5)
Pd(01)	N(3)	2.018(3)		C(30)	C(29)	1.387(5)

P(1)	O(3)	1.520(3)		C(31)	C(24)	1.398(5)
P(1)	O(1)	1.556(3)		C(2)	C(1)	1.390(5)
P(1)	O(2)	1.516(3)		C(12)	C(13)	1.387(5)
P(1)	C(6)	1.801(4)		C(39)	C(40)	1.385(5)
P(2)	O(5)	1.503(3)		C(39)	C(38)	1.394(5)
P(2)	O(4)	1.510(3)		C(24)	C(23)	1.396(5)
P(2)	O(6)	1.564(3)		C(8)	C(7)	1.394(5)
P(2)	C(17)	1.791(4)		C(36)	C(35)	1.493(5)
P(4)	O(10)	1.490(3)		C(36)	C(41)	1.393(5)
P(4)	O(11)	1.561(3)		C(36)	C(37)	1.389(5)
P(4)	O(12)	1.521(3)		C(35)	C(42)	1.402(5)
P(4)	C(39)	1.806(4)		C(17)	C(18)	1.398(9)
P(3)	O(8)	1.511(3)		C(17)	C(16)	1.405(9)
P(3)	O(7)	1.525(3)		C(17)	C(16A)	1.411(10)
P(3)	O(9)	1.572(3)		C(17)	C(18A)	1.338(13)
P(3)	C(28)	1.798(4)		C(4)	C(5)	1.389(5)
N(4)	C(34)	1.382(4)		C(41)	C(40)	1.380(5)
N(4)	C(31)	1.379(4)		C(13)	C(20)	1.392(5)
N(2)	C(9)	1.370(5)		C(13)	C(14)	1.498(5)
N(2)	C(12)	1.372(5)		C(20)	C(21)	1.431(6)
N(2S)	C(4S)	1.475(5)		C(14)	C(19)	1.384(9)
N(2S)	C(3S)	1.478(5)		C(14)	C(15)	1.364(9)
N(1)	C(42)	1.385(5)		C(14)	C(15A)	1.454(11)
N(1)	C(1)	1.377(5)		C(14)	C(19A)	1.325(12)
N(3)	C(20)	1.384(5)		C(23)	C(22)	1.437(5)
N(3)	C(23)	1.373(5)		C(42)	C(43)	1.439(5)
N(1S)	C(2S)	1.475(5)		C(37)	C(38)	1.390(5)
N(1S)	C(1S)	1.475(5)		C(1)	C(44)	1.438(5)
C(28)	C(27)	1.380(5)		C(43)	C(44)	1.345(6)
C(28)	C(29)	1.393(5)		C(22)	C(21)	1.357(6)
C(34)	C(33)	1.439(5)		C(18)	C(19)	1.401(10)
C(34)	C(35)	1.393(5)		C(16)	C(15)	1.382(12)
C(6)	C(5)	1.392(5)		C(15A)	C(16A)	1.416(12)
C(6)	C(7)	1.381(5)		C(18A)	C(19A)	1.419(15)
C(10)	C(9)	1.438(5)		N(3S)	C(5S)	1.401(8)
C(10)	C(11)	1.347(6)		N(3S)	C(6S)	1.574(11)
C(25)	C(30)	1.392(5)		O(2S)	C(12S)	1.259(14)
C(25)	C(24)	1.492(5)		N(5S)	C(11S)	1.392(14)
C(25)	C(26)	1.395(5)		N(5S)	C(12S)	1.316(15)
C(9)	C(2)	1.395(5)		N(5S)	C(10S)	1.471(15)

C(3)	C(2)	1.495(5)		O(1S)	C(9S)	1.250(15)
C(3)	C(8)	1.386(5)		N(4S)	C(9S)	1.374(16)
C(3)	C(4)	1.396(5)		N(4S)	C(7S)	1.330(18)
C(32)	C(33)	1.341(5)		N(4S)	C(8S)	1.47(2)

Table S3. Bond angles for **HOF-IPCE-1Pd**.

Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
N(4)	Pd(01)	N(2)	179.10(13)		N(2)	C(12)	C(11)	109.3(3)
N(1)	Pd(01)	N(4)	90.16(12)		N(2)	C(12)	C(13)	126.4(3)
N(1)	Pd(01)	N(2)	89.86(12)		C(13)	C(12)	C(11)	124.2(4)
N(1)	Pd(01)	N(3)	179.70(13)		C(30)	C(29)	C(28)	120.5(4)
N(3)	Pd(01)	N(4)	89.93(12)		C(40)	C(39)	P(4)	119.7(3)
N(3)	Pd(01)	N(2)	90.06(12)		C(40)	C(39)	C(38)	118.3(3)
O(3)	P(1)	O(1)	111.40(15)		C(38)	C(39)	P(4)	122.1(3)
O(3)	P(1)	C(6)	108.20(17)		C(31)	C(24)	C(25)	118.0(3)
O(1)	P(1)	C(6)	104.17(16)		C(23)	C(24)	C(25)	117.4(3)
O(2)	P(1)	O(3)	113.32(17)		C(23)	C(24)	C(31)	124.6(3)
O(2)	P(1)	O(1)	110.61(17)		C(3)	C(8)	C(7)	120.5(4)
O(2)	P(1)	C(6)	108.67(17)		C(41)	C(36)	C(35)	121.3(3)
O(5)	P(2)	O(4)	113.43(17)		C(37)	C(36)	C(35)	120.4(3)
O(5)	P(2)	O(6)	112.28(16)		C(37)	C(36)	C(41)	118.3(3)
O(5)	P(2)	C(17)	108.49(18)		C(34)	C(35)	C(36)	119.0(3)
O(4)	P(2)	O(6)	109.82(18)		C(34)	C(35)	C(42)	124.2(3)
O(4)	P(2)	C(17)	108.16(17)		C(42)	C(35)	C(36)	116.8(3)
O(6)	P(2)	C(17)	104.16(18)		C(18)	C(17)	P(2)	123.4(4)
O(10)	P(4)	O(11)	112.54(18)		C(18)	C(17)	C(16)	115.8(5)
O(10)	P(4)	O(12)	117.95(19)		C(16)	C(17)	P(2)	120.4(4)
O(10)	P(4)	C(39)	110.09(18)		C(16A)	C(17)	P(2)	115.0(5)
O(11)	P(4)	C(39)	106.19(18)		C(18A)	C(17)	P(2)	124.2(5)
O(12)	P(4)	O(11)	104.6(2)		C(18A)	C(17)	C(16A)	120.6(7)
O(12)	P(4)	C(39)	104.60(19)		C(5)	C(4)	C(3)	120.1(4)
O(8)	P(3)	O(7)	115.71(17)		C(4)	C(5)	C(6)	120.7(4)
O(8)	P(3)	O(9)	110.65(17)		C(27)	C(26)	C(25)	120.5(4)
O(8)	P(3)	C(28)	109.29(17)		C(40)	C(41)	C(36)	120.5(4)
O(7)	P(3)	O(9)	109.67(18)		C(6)	C(7)	C(8)	120.6(4)
O(7)	P(3)	C(28)	107.89(17)		C(12)	C(13)	C(20)	124.2(4)
O(9)	P(3)	C(28)	102.80(17)		C(12)	C(13)	C(14)	117.2(3)
C(34)	N(4)	Pd(01)	127.0(2)		C(20)	C(13)	C(14)	118.5(4)
C(31)	N(4)	Pd(01)	126.9(2)		C(41)	C(40)	C(39)	121.5(4)
C(31)	N(4)	C(34)	106.1(3)		N(3)	C(20)	C(13)	126.2(4)

C(9)	N(2)	Pd(01)	126.5(2)		N(3)	C(20)	C(21)	109.5(3)
C(9)	N(2)	C(12)	106.9(3)		C(13)	C(20)	C(21)	124.3(4)
C(12)	N(2)	Pd(01)	126.5(2)		C(19)	C(14)	C(13)	121.0(5)
C(4S)	N(2S)	C(3S)	112.6(3)		C(15)	C(14)	C(13)	119.1(5)
C(42)	N(1)	Pd(01)	126.8(2)		C(15)	C(14)	C(19)	119.2(6)
C(1)	N(1)	Pd(01)	127.0(3)		C(15A)	C(14)	C(13)	116.7(5)
C(1)	N(1)	C(42)	106.2(3)		C(19A)	C(14)	C(13)	125.1(6)
C(20)	N(3)	Pd(01)	126.3(3)		C(19A)	C(14)	C(15A)	117.9(6)
C(23)	N(3)	Pd(01)	127.3(3)		N(3)	C(23)	C(24)	125.5(3)
C(23)	N(3)	C(20)	106.3(3)		N(3)	C(23)	C(22)	109.8(3)
C(2S)	N(1S)	C(1S)	113.0(4)		C(24)	C(23)	C(22)	124.5(4)
C(27)	C(28)	P(3)	122.5(3)		N(1)	C(42)	C(35)	125.9(3)
C(27)	C(28)	C(29)	118.9(3)		N(1)	C(42)	C(43)	109.4(3)
C(29)	C(28)	P(3)	118.6(3)		C(35)	C(42)	C(43)	124.7(4)
N(4)	C(34)	C(33)	109.3(3)		C(36)	C(37)	C(38)	121.0(4)
N(4)	C(34)	C(35)	125.9(3)		C(37)	C(38)	C(39)	120.4(4)
C(35)	C(34)	C(33)	124.7(3)		N(1)	C(1)	C(2)	126.1(3)
C(5)	C(6)	P(1)	121.2(3)		N(1)	C(1)	C(44)	109.5(3)
C(7)	C(6)	P(1)	119.7(3)		C(2)	C(1)	C(44)	124.4(4)
C(7)	C(6)	C(5)	119.1(3)		C(44)	C(43)	C(42)	107.3(4)
C(11)	C(10)	C(9)	107.4(3)		C(21)	C(22)	C(23)	107.0(4)
C(30)	C(25)	C(24)	120.4(3)		C(43)	C(44)	C(1)	107.6(4)
C(30)	C(25)	C(26)	118.4(3)		C(22)	C(21)	C(20)	107.4(4)
C(26)	C(25)	C(24)	121.1(3)		C(17)	C(18)	C(19)	121.5(7)
N(2)	C(9)	C(10)	109.1(3)		C(14)	C(19)	C(18)	119.3(7)
N(2)	C(9)	C(2)	126.7(3)		C(15)	C(16)	C(17)	121.9(7)
C(2)	C(9)	C(10)	124.2(3)		C(14)	C(15)	C(16)	120.1(7)
C(8)	C(3)	C(2)	120.0(3)		C(16A)	C(15A)	C(14)	119.6(8)
C(8)	C(3)	C(4)	119.1(3)		C(17)	C(16A)	C(15A)	118.6(8)
C(4)	C(3)	C(2)	120.9(3)		C(17)	C(18A)	C(19A)	120.2(9)
C(33)	C(32)	C(31)	107.2(3)		C(14)	C(19A)	C(18A)	122.7(9)
C(28)	C(27)	C(26)	120.8(4)		C(5S)	N(3S)	C(6S)	116.0(7)
C(32)	C(33)	C(34)	107.7(3)		C(11S)	N(5S)	C(10S)	121.6(11)
C(10)	C(11)	C(12)	107.2(3)		C(12S)	N(5S)	C(11S)	119.9(10)
C(29)	C(30)	C(25)	120.8(4)		C(12S)	N(5S)	C(10S)	118.4(12)
N(4)	C(31)	C(32)	109.6(3)		O(2S)	C(12S)	N(5S)	127.7(12)
N(4)	C(31)	C(24)	125.6(3)		C(9S)	N(4S)	C(8S)	118.6(14)
C(24)	C(31)	C(32)	124.7(3)		C(7S)	N(4S)	C(9S)	125.3(15)
C(9)	C(2)	C(3)	117.7(3)		C(7S)	N(4S)	C(8S)	116.1(14)
C(1)	C(2)	C(9)	123.7(3)		O(1S)	C(9S)	N(4S)	129.1(13)

C(1)	C(2)	C(3)	118.6(3)					

Table S4. Hydrogen bonds for **HOF-IPCE-1Pd**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O(1)	H(1)	O(5)[1]	0.84	1.65	2.491(4)	175.6
O(11)	H(11)	O(4)[2]	0.84	1.75	2.537(4)	156.2
O(6)	H(6)	O(3)[3]	0.84	1.70	2.529(4)	167.5
O(9)	H(9)	O(2)[4]	0.84	1.69	2.522(4)	169.5
N(2S)	H(2SA)	O(3)[5]	0.91	1.89	2.765(4)	162.0
N(2S)	H(2SB)	O(2)[6]	0.91	1.83	2.735(4)	170.7
O(12)	H(12)	O(7)[1]	0.84	1.68	2.441(4)	148.6
N(1S)	H(1SA)	O(4)[7]	0.91	1.88	2.759(4)	161.4
N(1S)	H(1SB)	O(10)[8]	0.91	1.81	2.709(4)	171.6
N(3S)	H(3SE)	O(8)[9]	0.91	1.80	2.690(7)	165.3

[1]1+X,-1+Y,+Z; [2]1+X,+Y,-1+Z; [3]-1+X,1+Y,+Z; [4]-1+X,1+Y,-1+Z; [5]+X,1+Y,-1+Z; [6]1-X,1-Y,1-Z; [7]+X,+Y,-1+Z; [8]1-X,1-Y,-Z; [9]-X,2-Y,1-Z

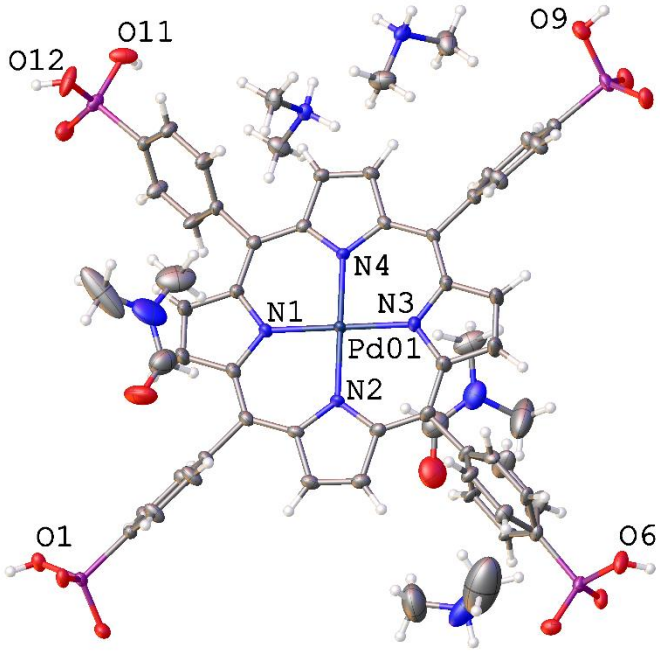


Figure S11. Asymmetric unit of **HOF-IPCE-1Pd**. (Pd: dark blue spheres, C: gray spheres, O: red spheres, N: blue spheres, P: orange spheres). Hydrogen atoms of porphyrin molecule and phenyl rings are omitted for the clarity.

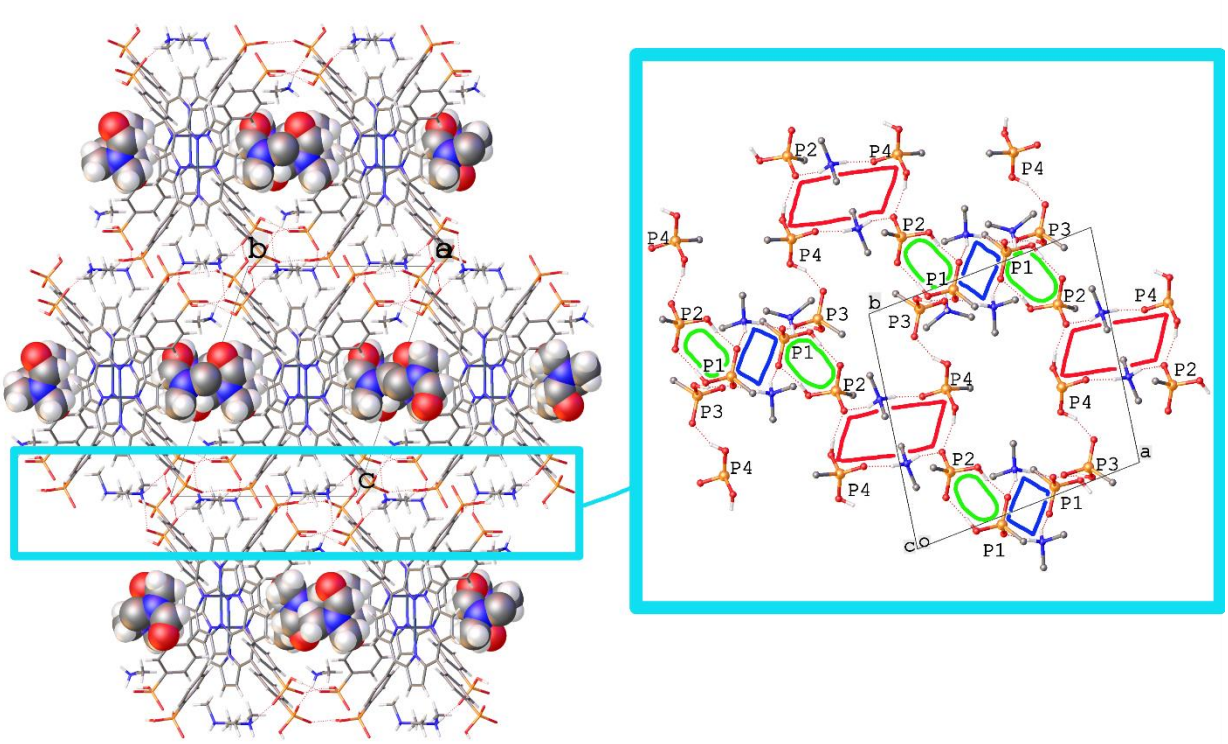
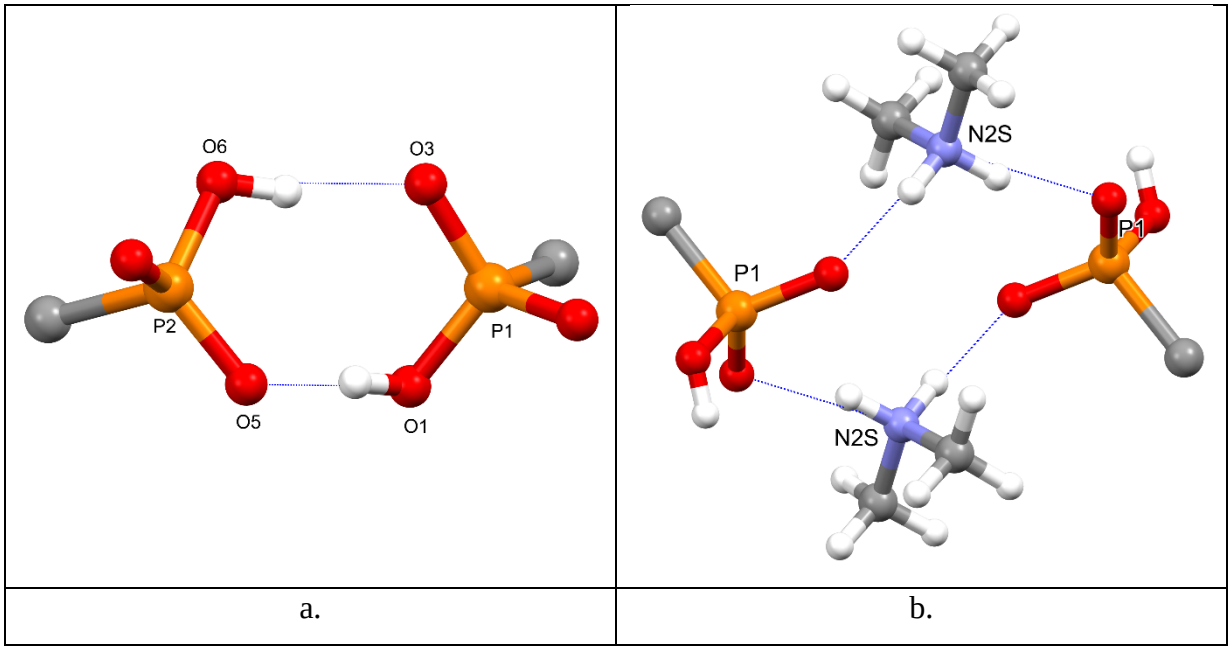
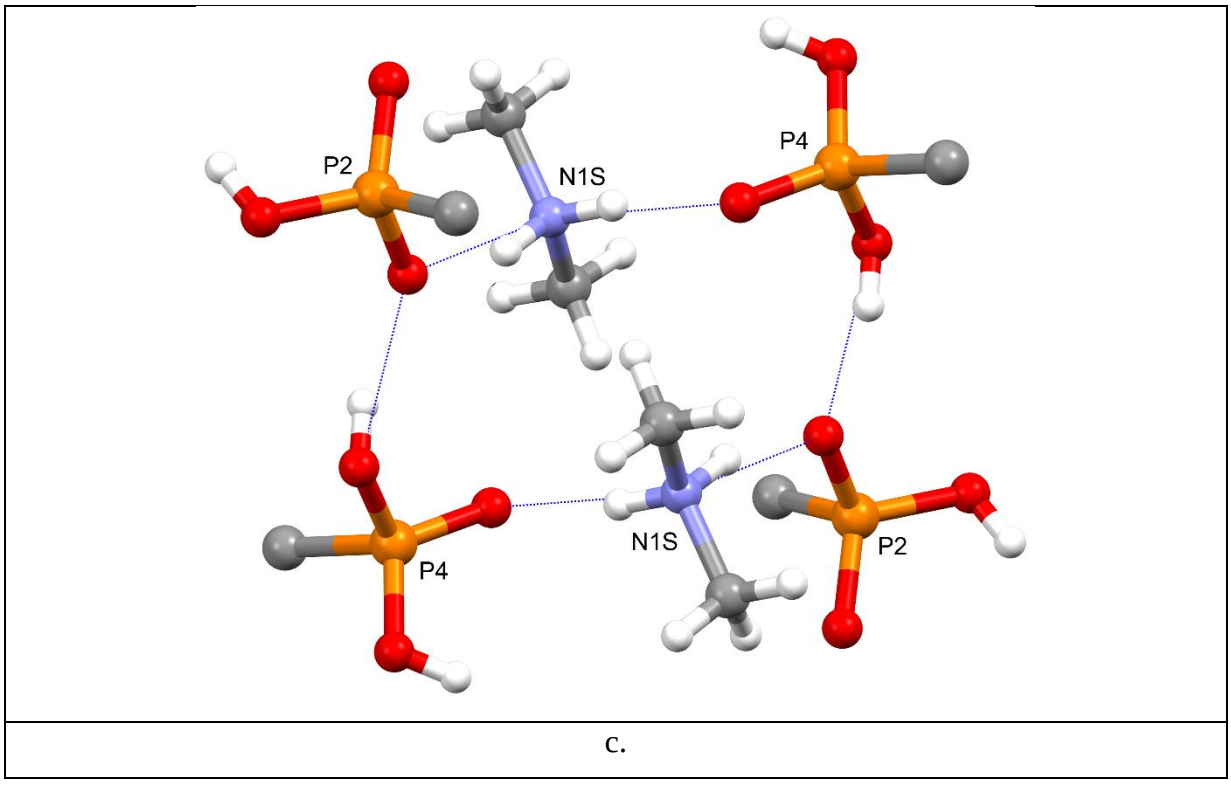


Figure S12. Packing of **HOF-IPCE-1Pd**. View along [100]. DMF molecules are shown by sphere packing. View along [001] on hydrogen-bonded 2D layer (the blue frame).

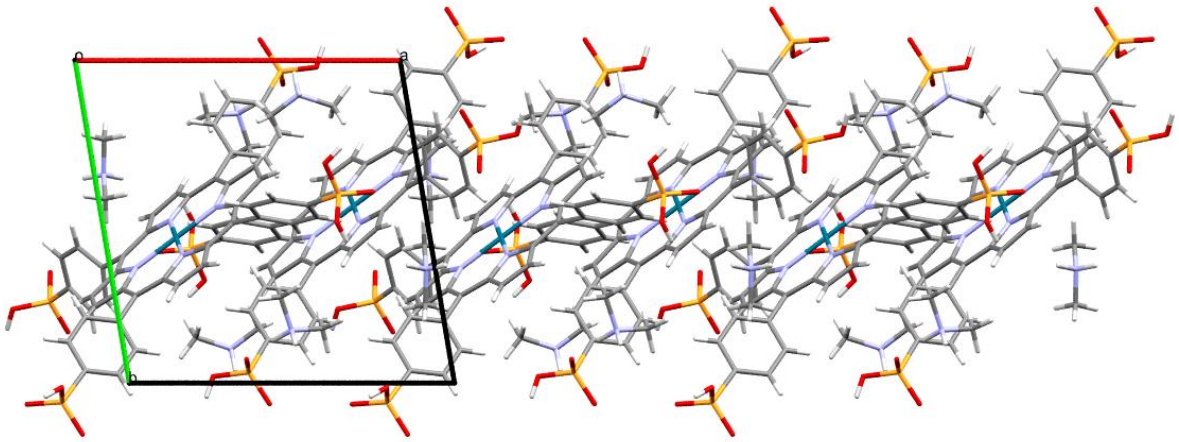


a. b.



c.

Figure S13. Graphical representation of hydrogen bonds of phosphonate groups of **Pd-H_5TPPP^{3-}** in **HOF-IPCE-1Pd**.



a.

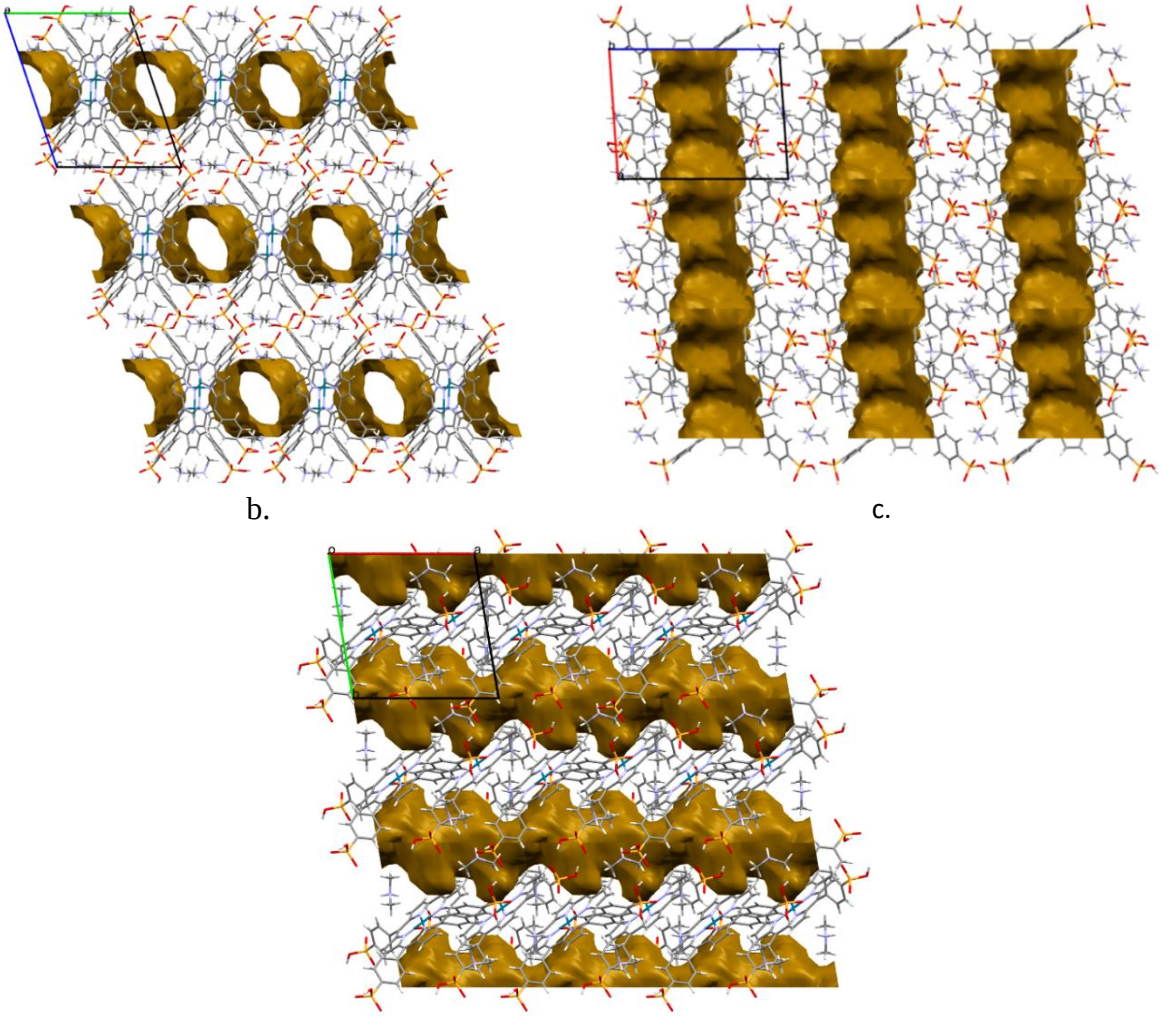


Figure S14. 3D packing of **HOF-IPCE-1Pd** a) one porphyrin stack along *a*, view along [001], b) 1D open channels along a, view along [100] direction, c) 1D open channels along a, view along [010] direction, d) 1D open channels along a, view along [001] direction.

Table S5. Comparison of channels size for several porphyrin-based HOFs.

	Di	Df	Dif	Dimensionality	Reference
IPCE-HOF-1Pd	5.8	3.8	5.8	1	This paper
GTUB5	5.4	4.9	5.4	1	[1]
H_2TPPA	6.0	4.1	6.0	1	[2]
HOF-7	8.8	5.8	8.8	3	[3]
HOF-6	7.8	5.2	7.8	3	[4]

PXRD patterns of HOF-IPCE-1Pd in different solvents

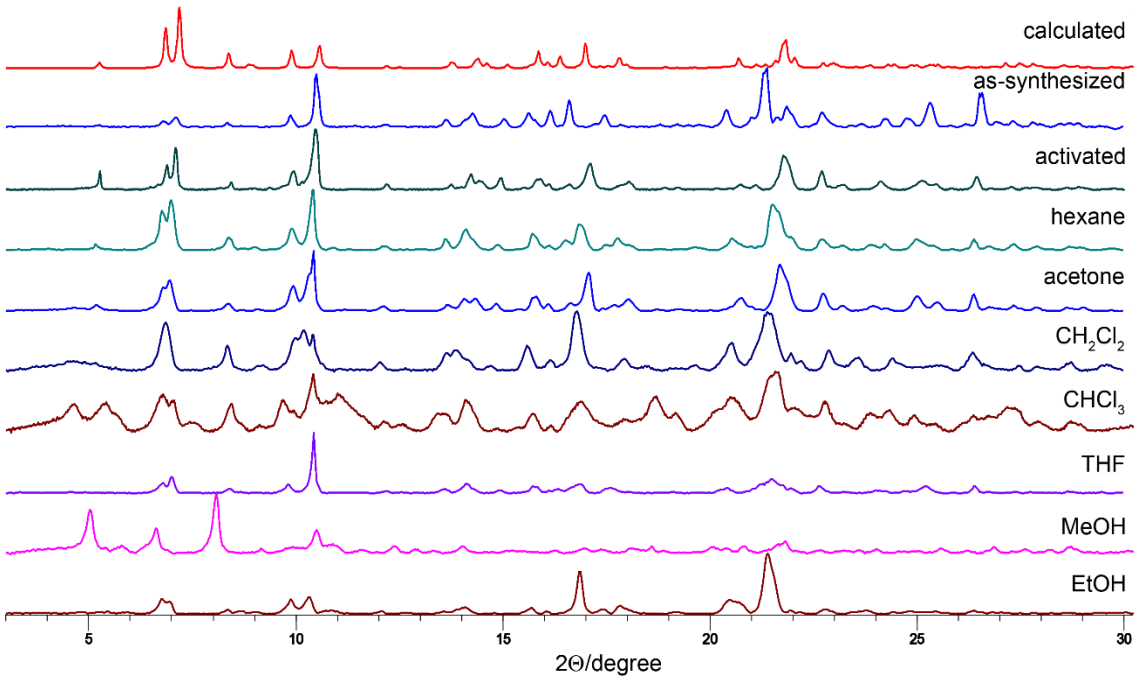


Figure S15. PXRD patterns of **HOF-IPCE-1Pd** treated by immersion in different solvents for 7 days.

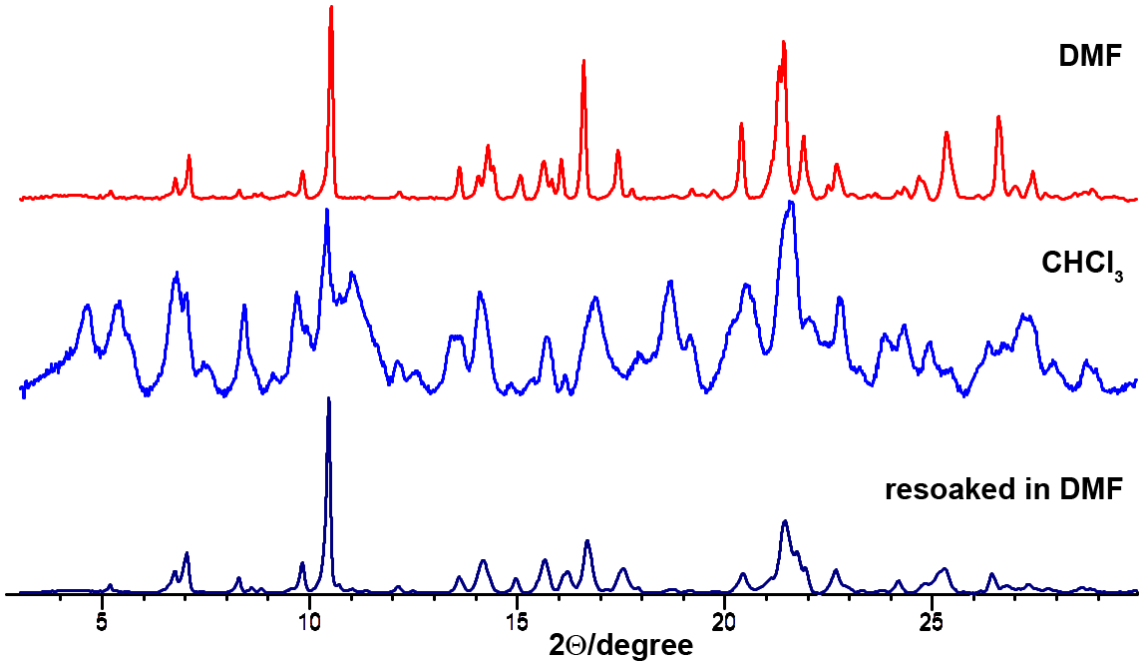


Figure S16. PXRD patterns of **HOF-IPCE-1Pd** treated by immersion in DMF and chloroform in comparison with data recorded for a sample re-soaked in DMF.

Pawley-refinements of HOF-IPCE-1Pd immersed in various solvents

For all samples of **HOF-IPCE-1Pd** immersed in various solvents, the triclinic unit cell dimensions and space group P-1 were tested in Pawley fits[5] with the program *MRIA*[6]. The unit cell dimensions are shown in **Table S6**.

Table S6. The triclinic unit cell parameters of **HOF-IPCE-1Pd** immersed in different solvents obtained in the Pawley fitting of the powder patterns measured in 3 – 30° 2θ range.

	a, Å	*b*, Å	*c*, Å	α, °	β, °	γ, °
DMF	13.247(5)	14.088(7)	17.991(9)	69.63(6)	82.20(9)	77.17(8)
HOF-IPCE-1Pd (activated sample)	12.937(4)	13.932(4)	18.042(7)	69.62(5)	82.47(7)	78.92(6)
hexane	13.006(6)	14.108(8)	18.097(10)	69.11(7)	81.95(9)	77.99(9)
acetone	12.969(7)	14.037(8)	18.224(11)	68.74(7)	81.55(9)	77.83(8)
THF	12.986(11)	14.140(12)	18.108(17)	69.77(8)	81.90(13)	77.10(9)

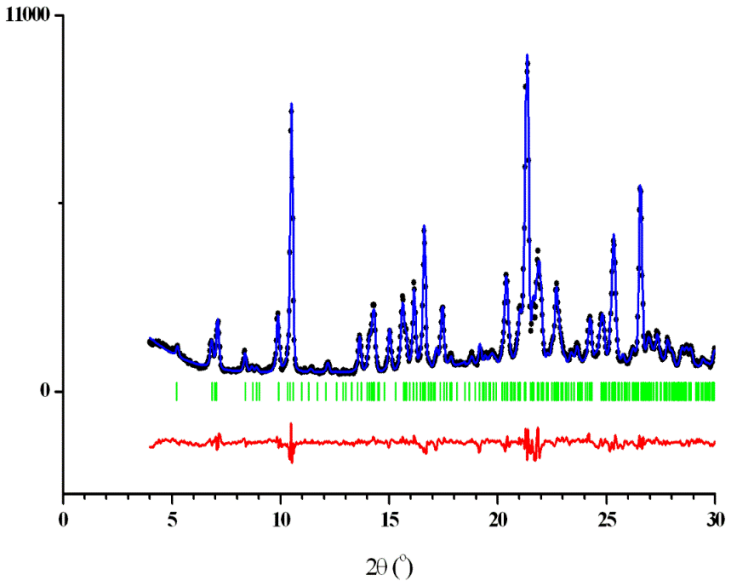


Figure S17. The result of the Pawley fitting of **HOF-IPCE-1Pd** kept in **DMF** showing the experimental (black dots), calculated (blue line) and difference (red line) profiles. The vertical green bars denote calculated positions of the diffraction peaks for the triclinic crystal structure.

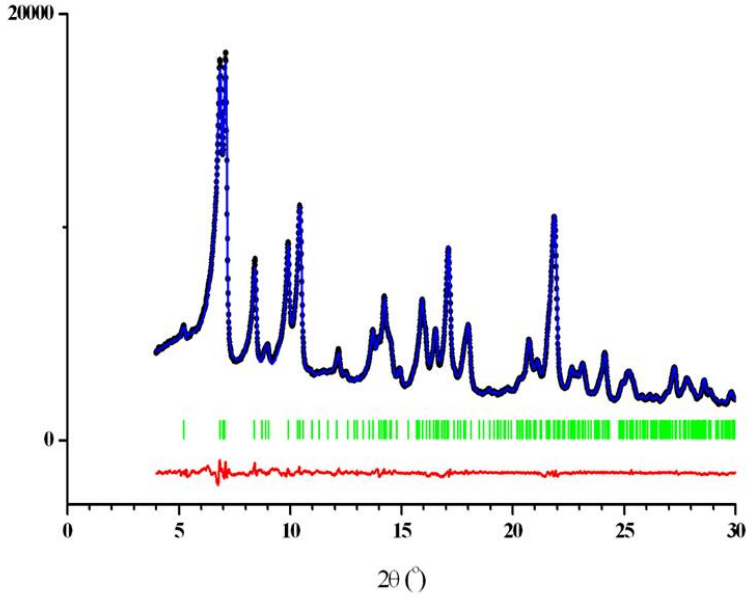


Figure S18. The result of the Pawley fitting of activated sample of **HOF-IPCE-1Pd** showing the experimental (black dots), calculated (blue line) and difference (red line) profiles. The vertical green bars denote calculated positions of the diffraction peaks for the triclinic crystal structure.

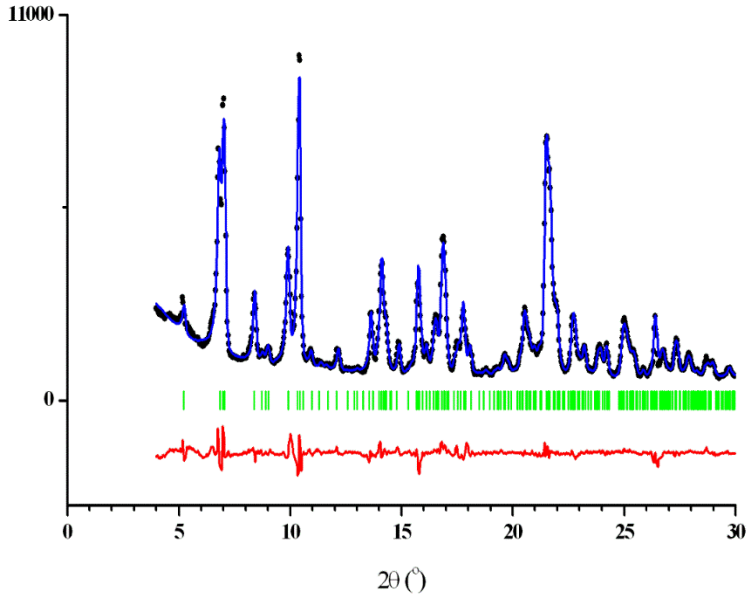


Figure S19. The result of the Pawley fitting of **HOF-IPCE-1Pd** kept in **hexane** showing the experimental (black dots), calculated (blue line) and difference (red line) profiles. The vertical green bars denote calculated positions of the diffraction peaks for the triclinic crystal structure.

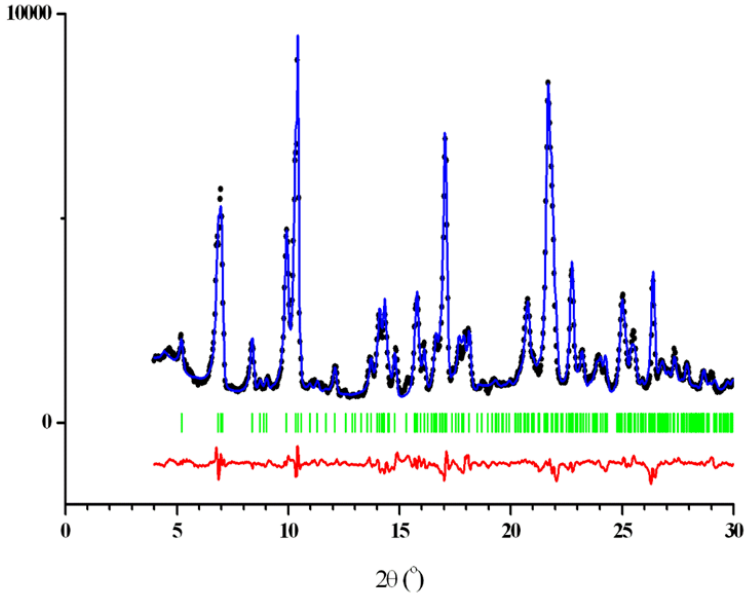


Figure S20. The result of the Pawley fitting of **HOF-IPCE-1Pd** kept in **acetone** showing the experimental (black dots), calculated (blue line) and difference (red line) profiles. The vertical green bars denote calculated positions of the diffraction peaks for the triclinic crystal structure.

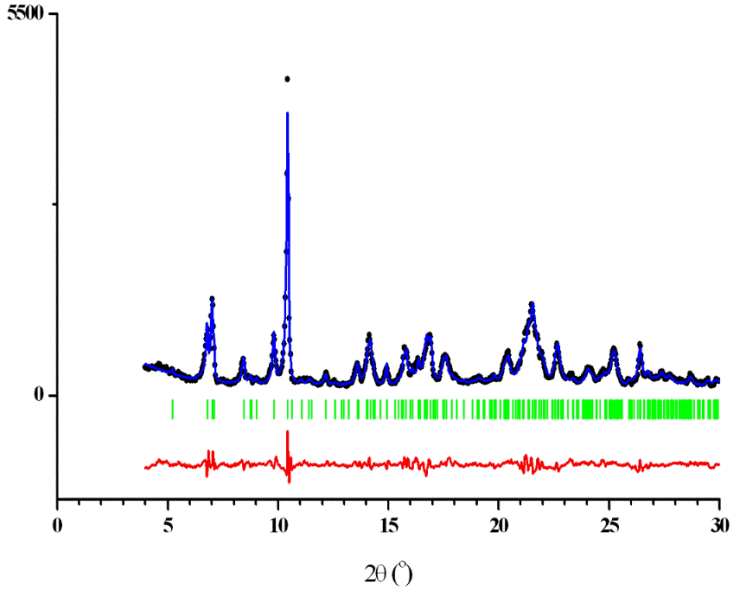


Figure S21. The result of the Pawley fitting of **HOF-IPCE-1Pd** kept in **THF** showing the experimental (black dots), calculated (blue line) and difference (red line) profiles. The vertical green bars denote calculated positions of the diffraction peaks for the triclinic crystal structure.

XPS data of HOF-IPCE-1Pd

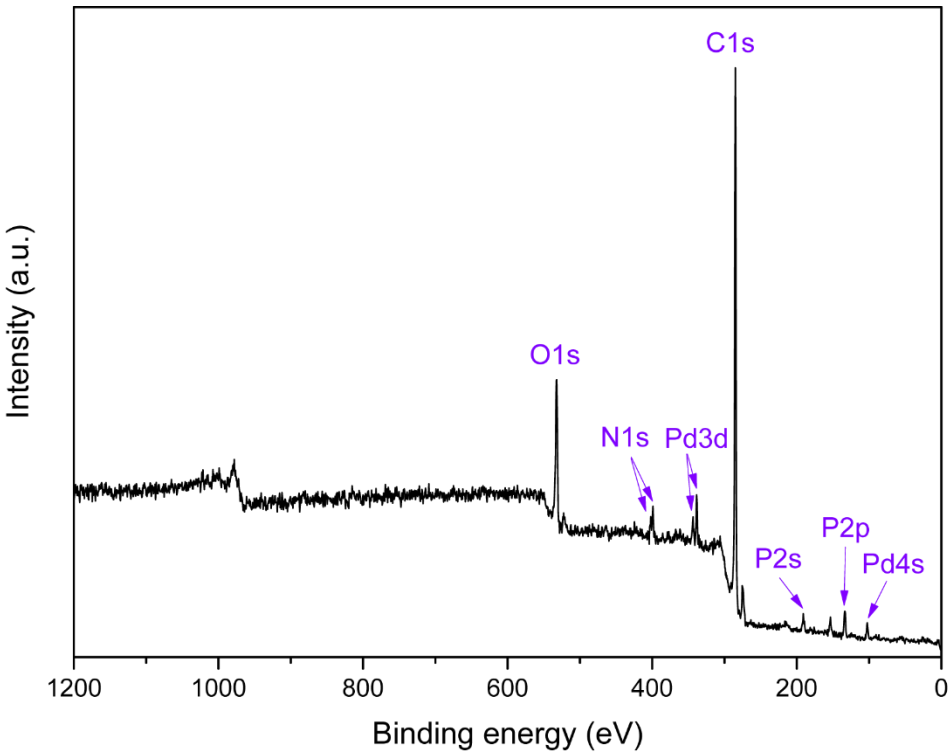
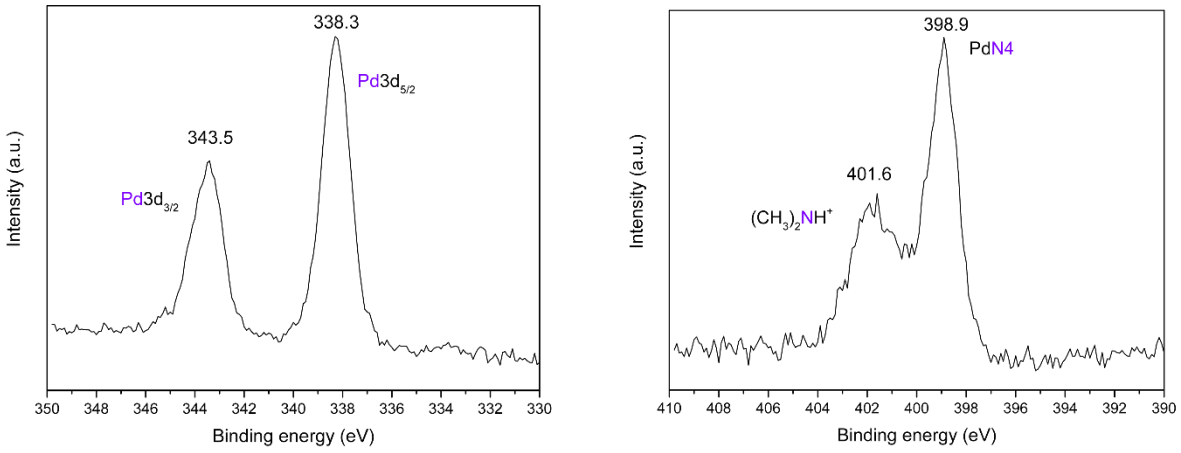
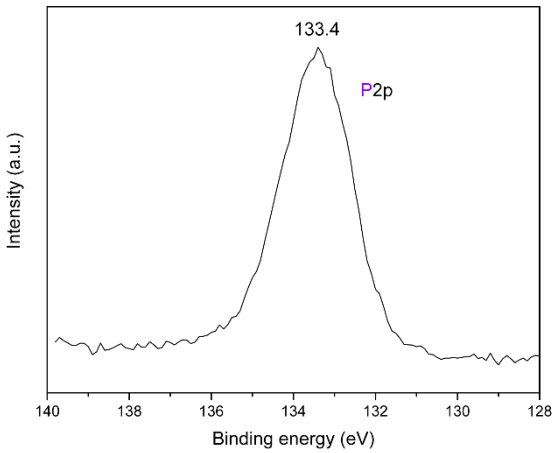


Figure S22. XPS spectrum of **HOF-IPCE-1Pd**.



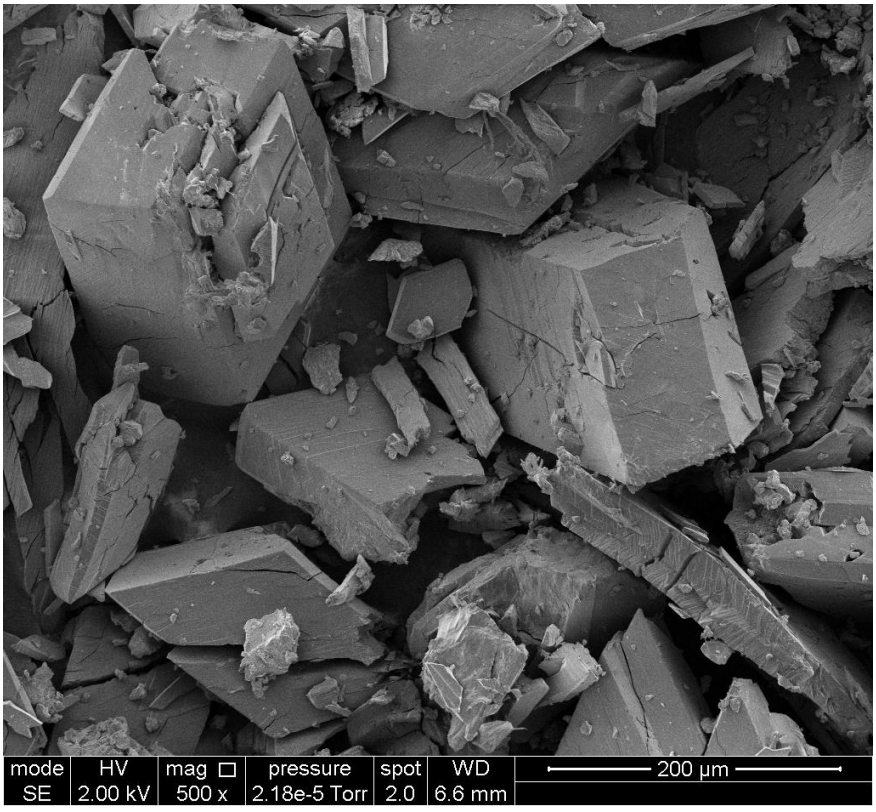
a. b.



c.

Figure S23. (a) XPS spectrum of Pd3d of **HOF-IPCE-1Pd**. (b) XPS spectrum of N1s of **HOF-IPCE-1Pd**. (c) XPS spectrum of P2p of **HOF-IPCE-1Pd**.

SEM and EDX data of HOF-IPCE-1Pd



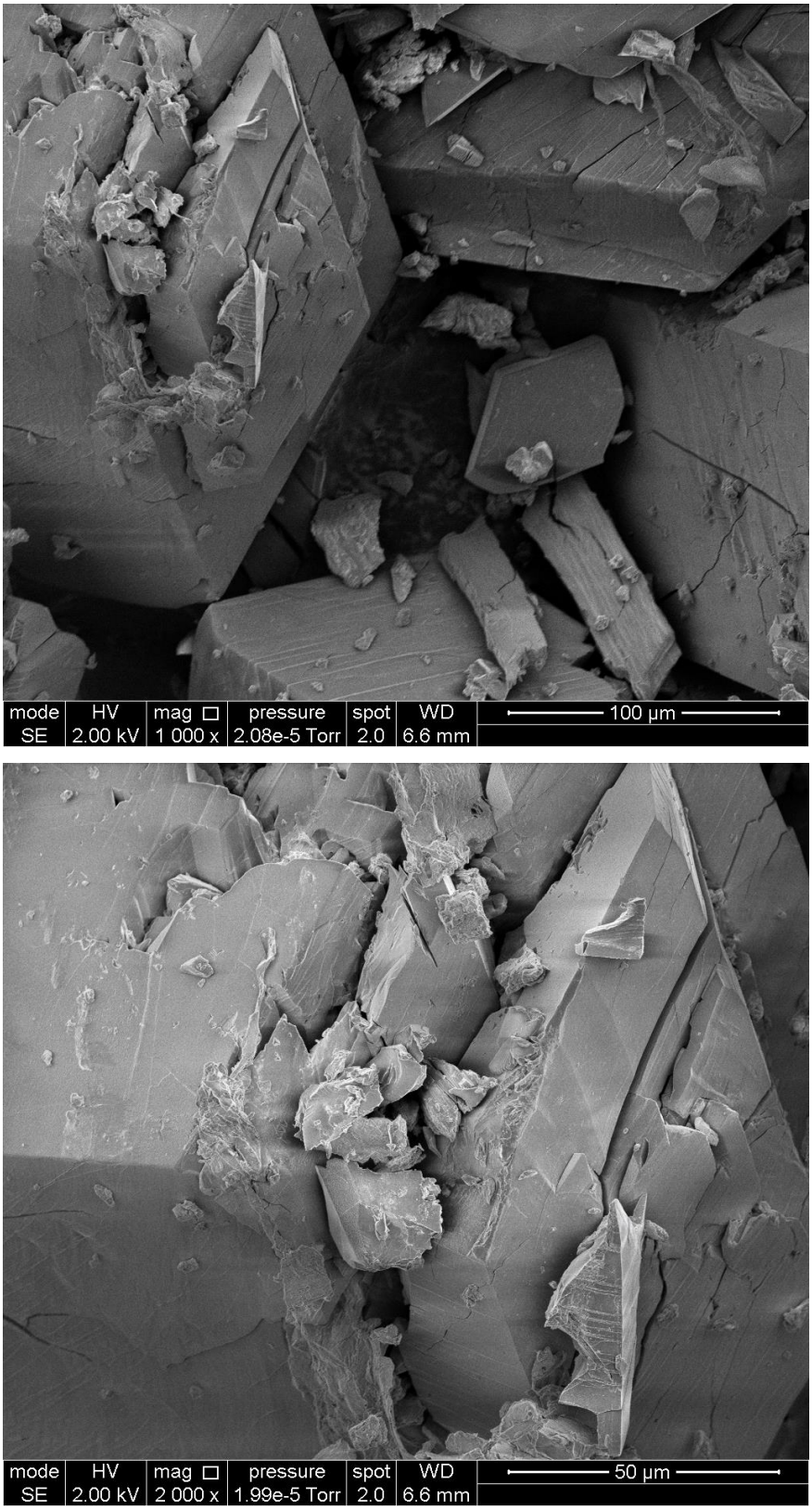


Figure S24. Typical scanning electron microscopy images of **HOF-IPCE-1Pd**.

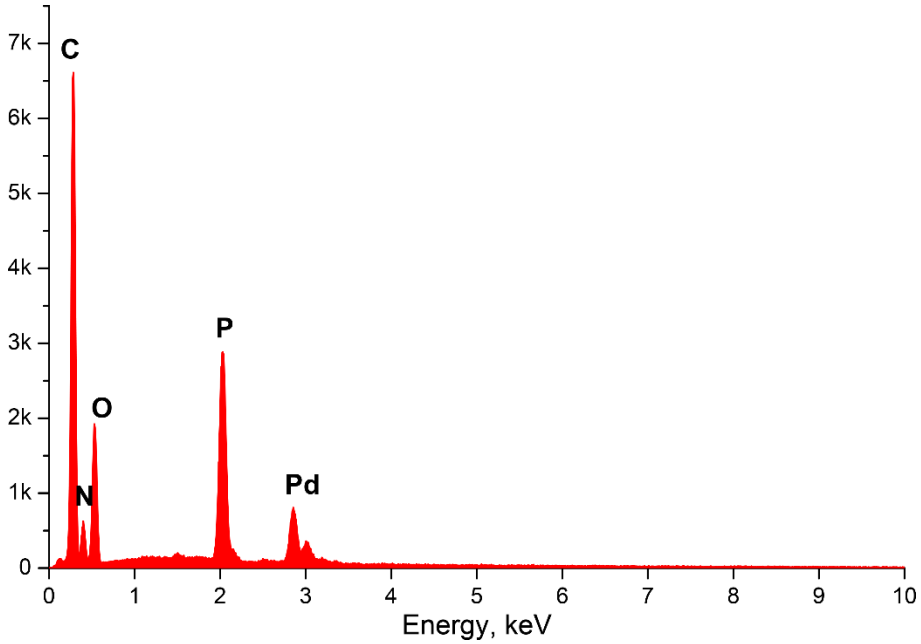


Figure S25. Typical EDX spectrum of **HOF-IPCE-1Pd**.

Table S7. Elemental analysis of **HOF-IPCE-1Pd** based on EDX spectroscopy data.

Element	C	N	O	P	Pd
Wt, %	57.9	10.2	20.2	06.1	05.6
At, %	68.3	10.4	17.9	02.8	00.8

Thermal stability of HOF-IPCE-1Pd

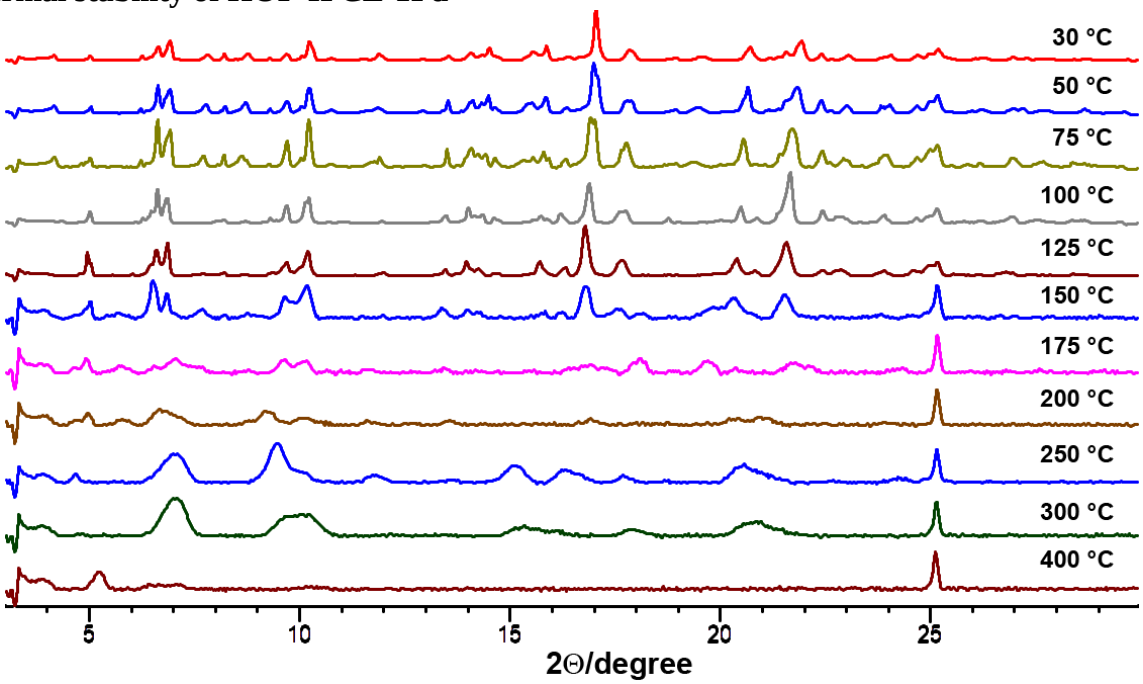


Figure S26. VT-PXRD patterns of **HOF-IPCE-1Pd** in the range of 30-400 °C.

TG investigations of HOF-IPCE-1Pd.

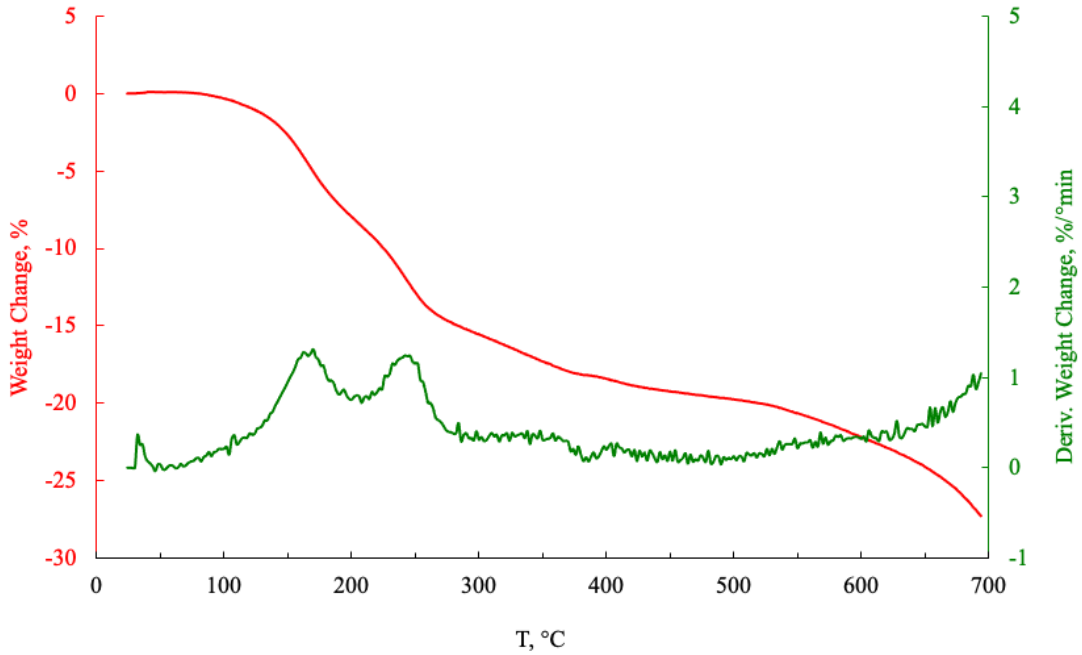


Figure S27. The TGA plot of **HOF-IPCE-1Pd**.

Sorption properties of HOF-IPCE-1Pd

As-synthesized material of **HOF-IPCE-1Pd** was soaked in dry acetone for 72 h during which time the solvent was replaced three times with fresh portions. After removing the acetone, the sample was activated under a dynamic vacuum at least for 6 h. The CO_2 adsorption−desorption isotherms were measured within the range of relative pressures from 10^{-4} to 0.995.

Table S8. The textural parameters of an activated sample of **HOF-IPCE-1Pd**.

Temperature of activation	**Specific surface area / $m^2 \cdot g^{-1}$**		**Pore volume / $cm^3 \cdot g^{-1}$**		**V_{ads}/ $cm^3(STP) \cdot g^{-1}$**
	BET	**DFT**	**Total**	**DFT**	
80 °C	160.2	77.7	0.114	0.078	53.9
100 °C	39.0	21.8	0.040	0.028	19.5

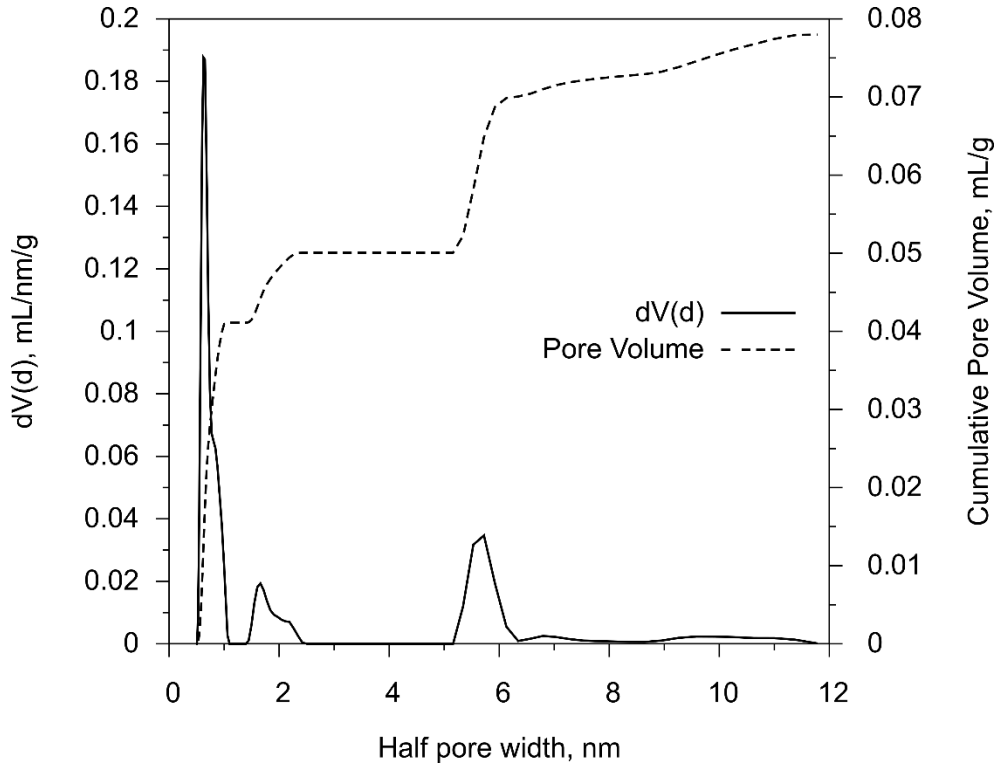


Figure S28. Pore size distribution curve for an activated sample of **HOF-IPCE-1Pd**.

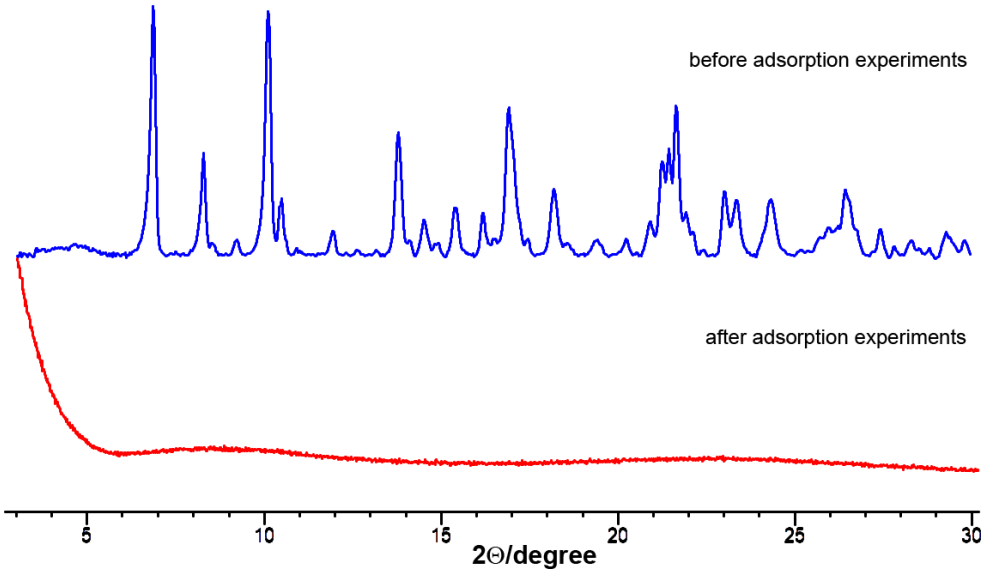
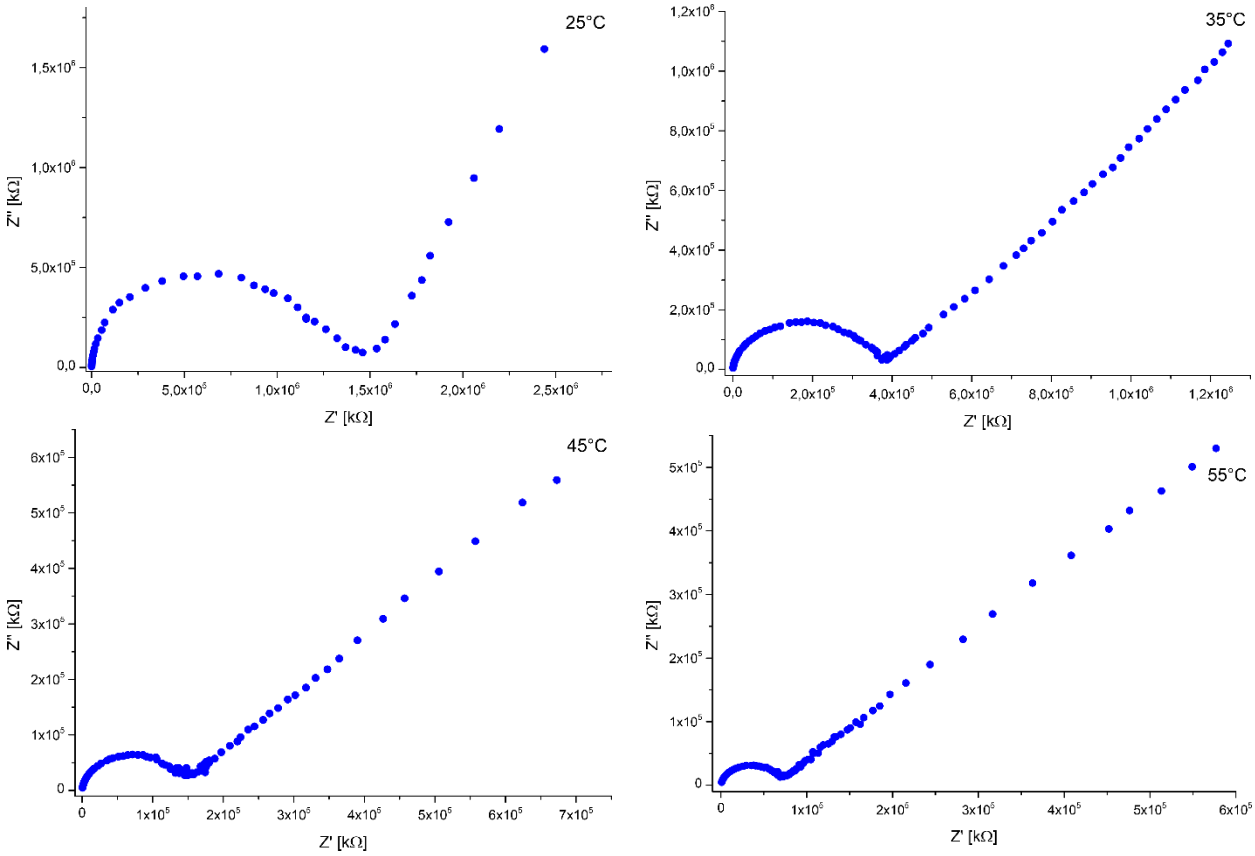


Figure S29. PXRD data for an activated sample of **HOF-IPCE-1Pd** before (the sample was activated at 80 °C) and after adsorption measurements.

Proton conductivity of HOF-IPCE-1Pd



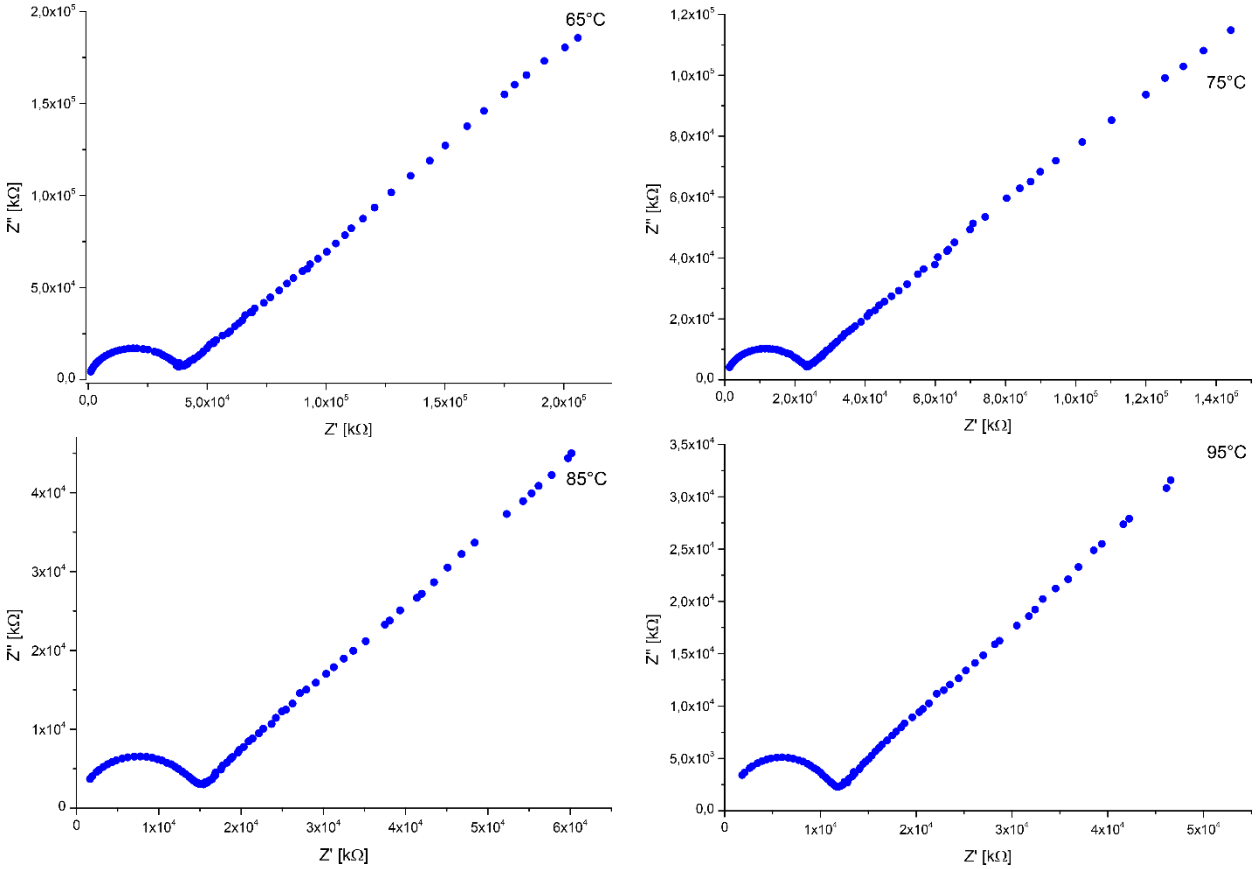
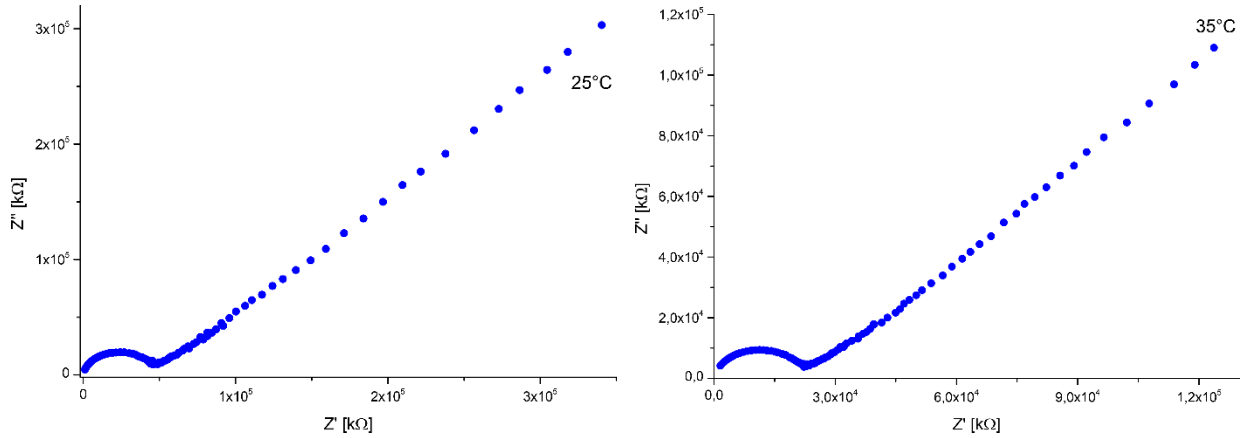


Figure S30. Nyquist plots of **HOF-IPCE-1Pd** at 32% RH and different temperatures.



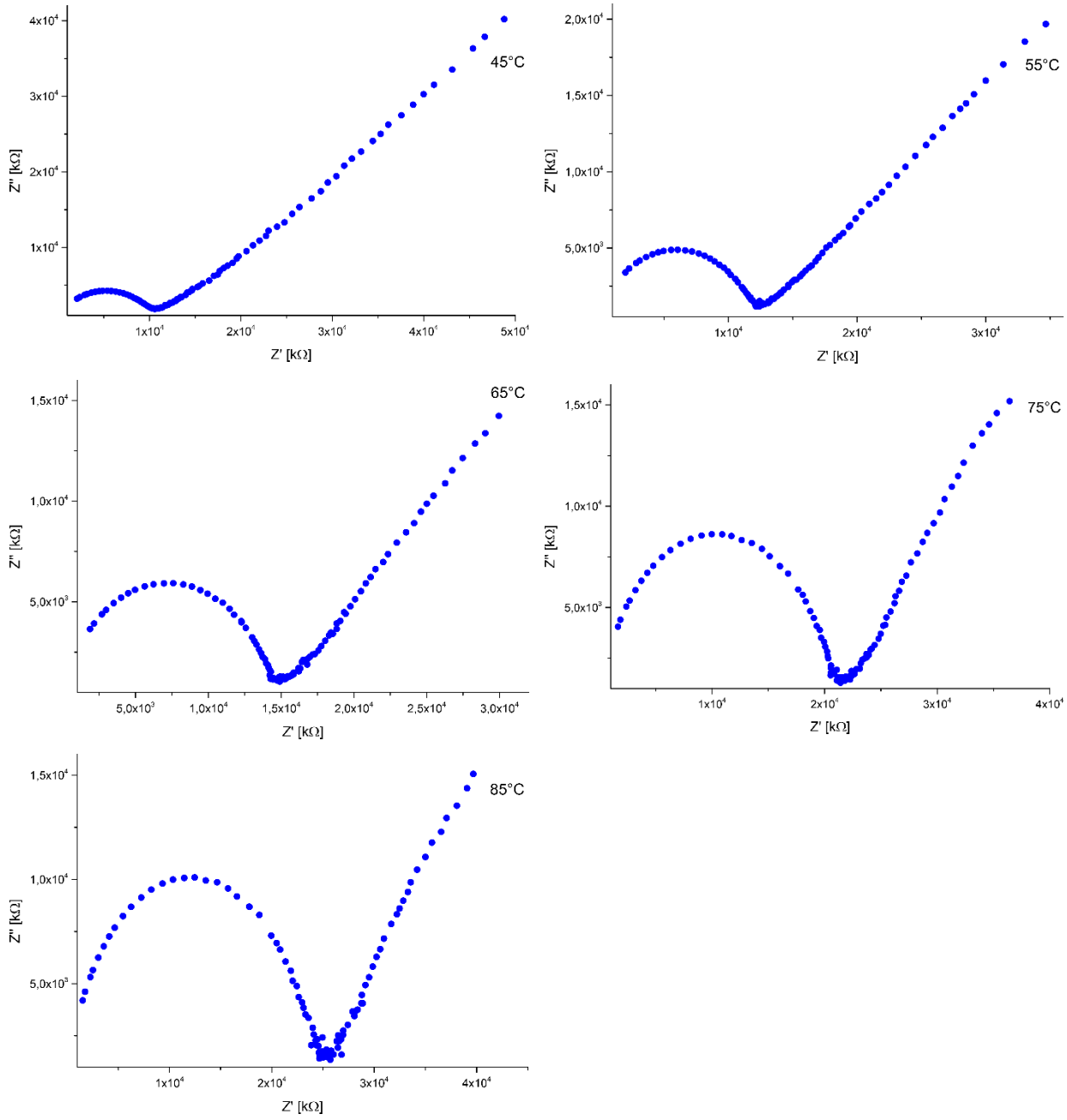


Figure S31. Nyquist plots of **HOF-IPCE-1Pd** at 60% RH and different temperatures.

PXRD data and Pawley-refinements of HOF-IPCE-1Pd-NH3

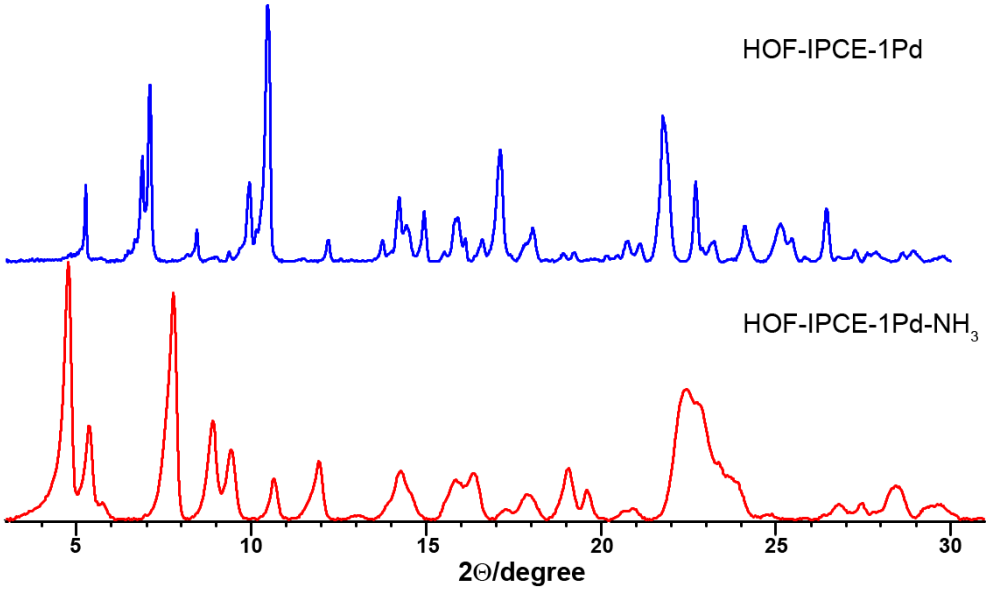


Figure S32. PXRD data for **HOF-IPCE-1Pd** and **HOF-IPCE-1Pd-NH3** samples.

For a sample **HOF-IPCE-1Pd-NH3** the triclinic unit cell dimensions and space group P-1 were tested in Pawley fits[5] with the program *MRIA*[6] (*Rp* = 0.025, *Rwp* = 0.059, *Rexp* = 0.014, GoF (Goodness of Fit) = 2.95).

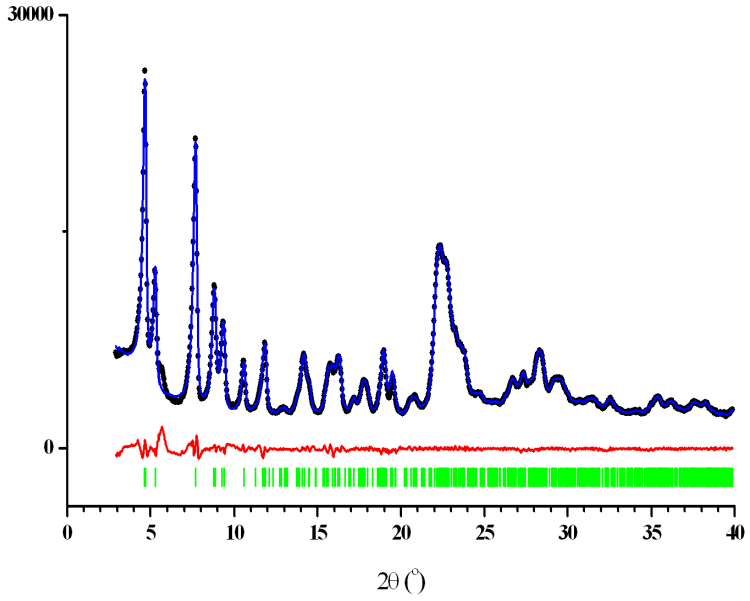


Figure S33. The result of the Pawley fitting of **HOF-IPCE-1Pd-NH3** showing the experimental (black dots), calculated (blue line) and difference (red line) profiles. The vertical green bars denote calculated positions of the diffraction peaks for the triclinic crystal structure.

TG investigations of HOF-IPCE-1Pd-NH$_3$

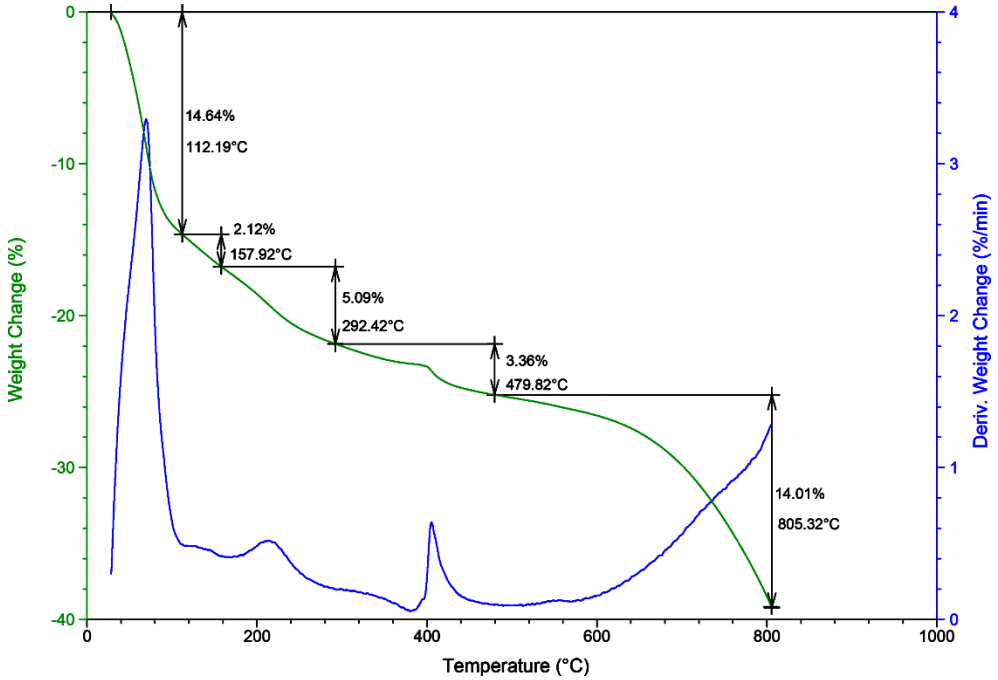


Figure S34. The TGA plot of **HOF-IPCE-1Pd-NH$_3$.**

IR spectrum of HOF-IPCE-1Pd-NH$_3$

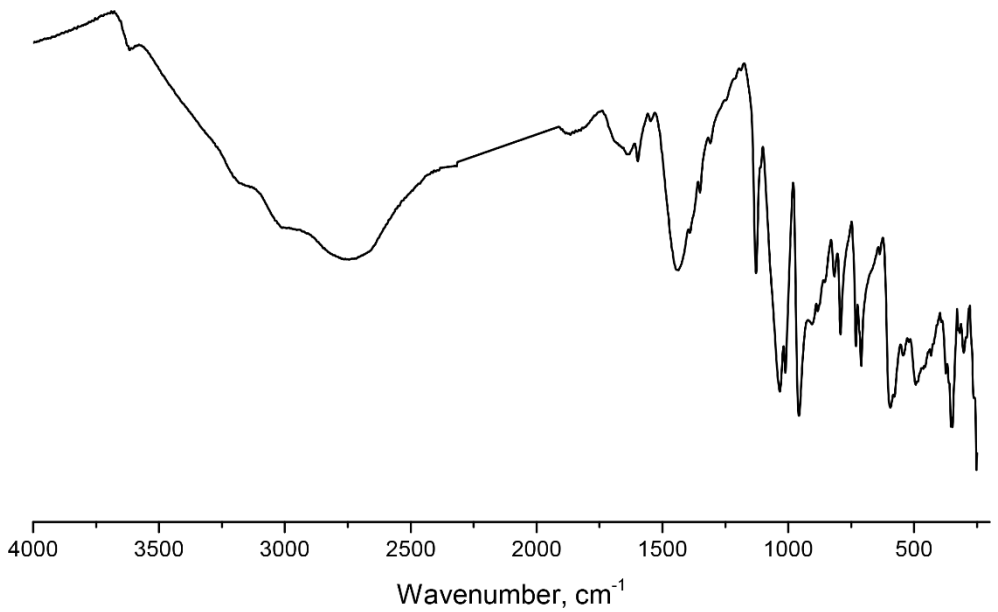
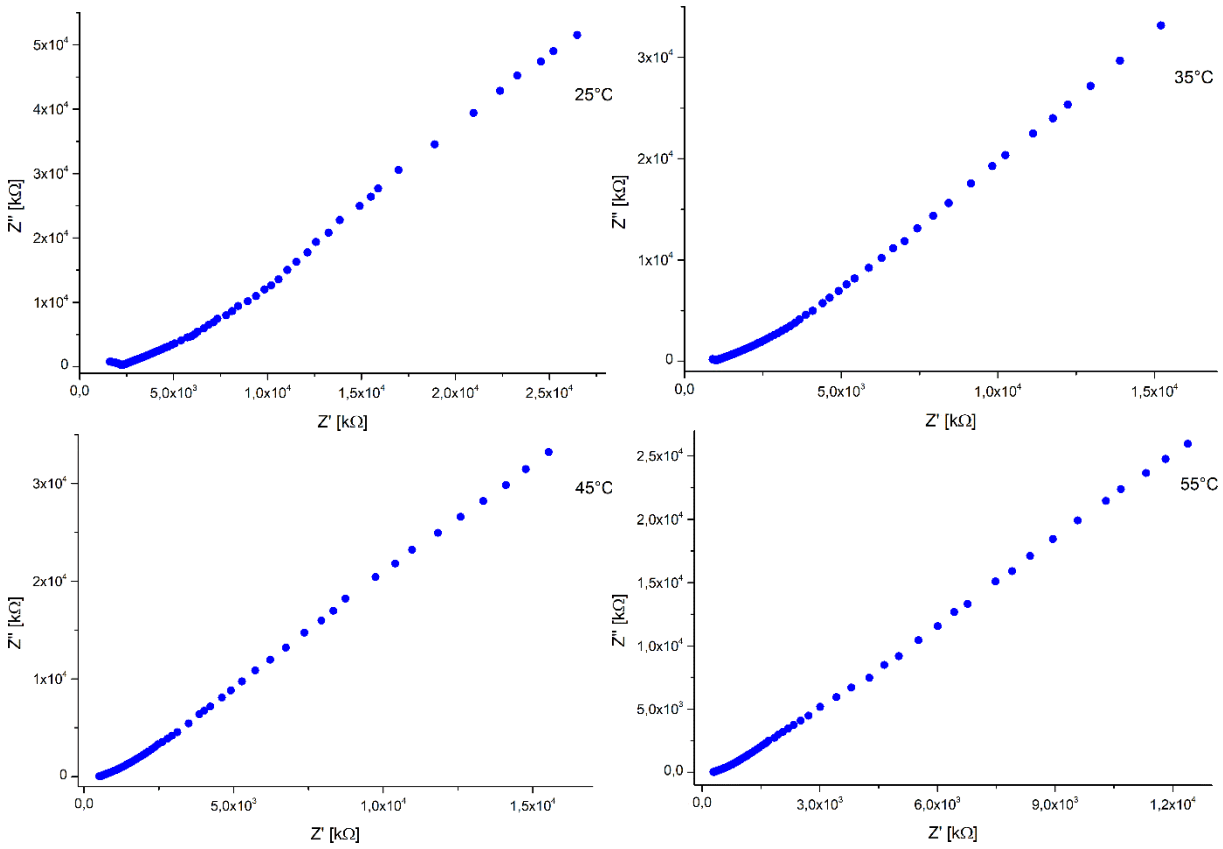


Figure S35. The IR spectrum of **HOF-IPCE-1Pd-NH$_3$**.

Proton conductivity of HOF-IPCE-1Pd-NH_3



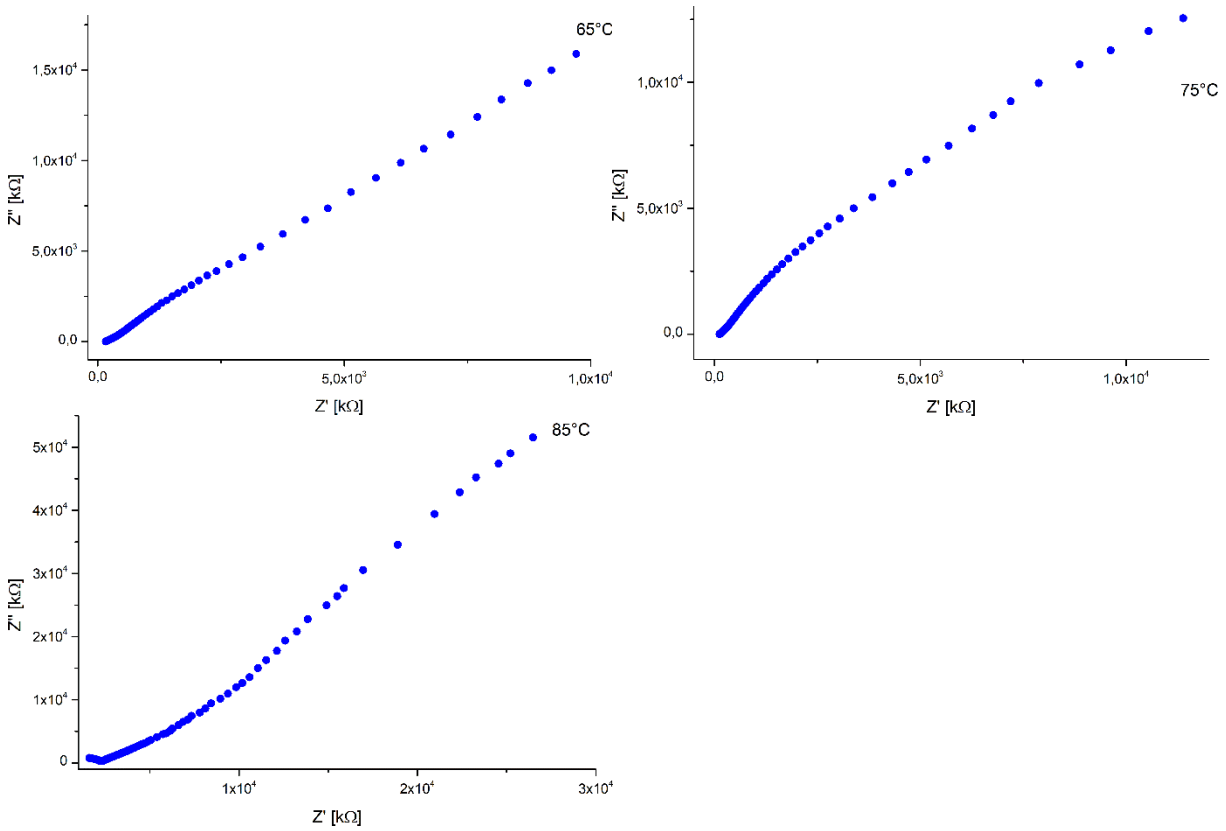


Figure S36. Nyquist plots of **HOF-IPCE-1Pd-NH$_3$** at 60% RH and different temperatures.

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4 W. Yang, F. Yang, T.-L. Hu, S. C. King, H. Wang, H. Wu, W. Zhou, J.-R. Li, H. D. Arman and B. Chen, *Cryst. Growth Des.*, 2016, **16**, 5831–5835.

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