Electronic Supporting Information

Proton Conductivity as a Function of the Metal Center in the Porphyrinylphosphonate-Based MOFs

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TABLE OF CONTENTS

Synthesis of IPCE-2Pd	2
Spectral characterization of compounds	
Structural characterization of IPCE-2Pd	
Topological analysis of IPCE-2Pd	
The morphology of IPCE-2Pd	17
EDS data of IPCE-2Pd	
XPS data of IPCE-2Pd	19
Sorption properties of IPCE-2Pd	
TG investigations of IPCE-2Pd	
Pawley-refinements of IPCE-2Pd at VT-PXRD experiments	
Structural characterization of IPCE-2Pd-HT	
PXRD patterns of IPCE-2Pd immersed in various solvents	
Pawley-refinements of IPCE-2Pd immersed in various solvents	
Proton conductivity of IPCE-2Pd	
REFERENCES	

Synthesis of IPCE-2Pd



Scheme S1. Synthetic route towards IPCE-2Pd. i: H(O)P(OEt)₂, Pd(OAc)₂/3PPh₃, Et₃N, toluene/EtOH mixture, reflux, 5 h; ii: CHCl₃/HCl, rt, 3 h, H₂-*m*TPPP (yield ~79%); iii: Pd(OAc)₂, CHCl₃/MeOH mixture, reflux, 30 min; iv: a) Me₃SiBr, DMF, 80 °C, 1 d, b) MeOH, rt, 1 d.

Spectral characterization of compounds



Figure S1. ¹H NMR spectrum of **Pd-***m***TPPP** (CDCl₃/MeOD 2:1, v/v). Solvent peaks are indicated with *($\delta_{\rm H}$ 7.26 ppm – CHCl₃, 4.17 ppm – DOH and H₂O, 3.12 ppm – CHD₂OD).



Figure S2. ³¹P{¹H} NMR spectrum of Pd-*m*TPPP (CDCl₃/MeOD 2:1, v/v).



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



Figure S4. UV-vis absorption spectrum of Pd-*m*TPPP in CH₂Cl₂ (c = 4.73 μ M).



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



Figure S6. ¹H NMR spectrum of **Pd-***m***H**₈**TPPP** (1 drop of a saturated solution of NaOH in D₂O) at 333 K. Solvent peak is indicated with *($\delta_{\rm H}$ 4.79 ppm – DOH and H₂O).



Figure S7. ${}^{31}P{}^{1}H$ NMR spectrum of Pd-*m*H₈TPPP (1 drop of a saturated solution of NaOH in D₂O) at 333 K.



Figure S8. IR spectrum of Pd-*m*H₈TPPP.



Figure S9. UV-vis absorption spectrum of Pd-*m*H₈TPPP in H₂O + 50 μ L of saturated solution of NaOH in H₂O (c = 6.33 μ M).



Figure S10. IR spectrum of IPCE-2Pd.

Structural characterization of IPCE-2Pd

Table S1. Bond lengths for IPCE-2Pd.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	$N1^1$	2.054(7)	C14	C15	1.378(14)
Pd1	N1	2.054(7)	C14	C19	1.400(18)
Pd1	N2 ¹	2.093(10)	C15	C16	1.407(15)
Pd1	N2	2.093(10)	C16	C17	1.397(17)
N1	C1	1.384(14)	C17	C18	1.370(14)
N1	C20	1.387(13)	C18	C19	1.379(15)
N2	C12	1.398(13)	C18	P2	1.795(13)
N2	С9	1.406(14)	C20	C21	1.445(13)
C1	C2	1.398(16)	C20	C13 ¹	1.591(17)
C1	C22	1.429(12)	C21	C22	1.343(17)
C2	С9	1.451(14)	P1	02	1.502(7)
C2	C3	1.488(16)	P1	03	1.517(7)
C3	C8	1.379(13)	P1	01	1.519(8)
C3	C4	1.403(17)	01	Zn1 ²	1.953(6)
C4	C5	1.374(16)	03	Zn1 ³	1.904(6)
C5	C6	1.399(13)	P2	06	1.469(7)
C5	P1	1.799(13)	P2	04	1.509(8)
C6	C7	1.382(17)	P2	05	1.544(7)
C7	C8	1.405(16)	04	Znl	1.897(8)
C9	C10	1.459(17)	06	Zn1 ⁴	1.981(6)
C10	C11	1.316(13)	Znl	O3 ³	1.904(6)
C11	C12	1.434(17)	Znl	O1 ⁵	1.953(6)
C12	C13	1.374(14)	Znl	O6 ⁴	1.981(6)
C13	C14	1.492(15)	N3	C24	1.428(14)
C13	$C20^1$	1.591(17)	 N3	C23	1.430(12)

¹1-X,1-Y,1-Z; ²-X,1/2+Y,3/2-Z; ³-X,1-Y,1-Z; ⁴-X,-Y,1-Z; ⁵-X,-1/2+Y,3/2-Z

Table S2. Bond angles for IPCE-2Pd.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1 ¹	Pd1	N1	180.0(3)	C15	C14	C19	120.3(10)
$N1^1$	Pd1	N2 ¹	88.4(3)	C15	C14	C13	121.4(11)
N1	Pd1	N2 ¹	91.6(3)	C19	C14	C13	118.1(9)
$N1^1$	Pd1	N2	91.6(3)	C14	C15	C16	120.0(11)
N1	Pd1	N2	88.4(3)	C17	C16	C15	118.7(9)
N2 ¹	Pd1	N2	180.0(3)	C18	C17	C16	120.6(10)
C1	N1	C20	104.3(7)	C17	C18	C19	120.9(11)
C1	N1	Pd1	129.5(7)	C17	C18	P2	110.3(8)
C20	N1	Pd1	126.3(7)	C19	C18	P2	128.8(8)
C12	N2	C9	104.0(9)	C18	C19	C14	119.4(9)
C12	N2	Pd1	128.2(7)	N1	C20	C21	110.6(10)
C9	N2	Pd1	127.6(6)	N1	C20	C13 ¹	123.8(8)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C1	C2	124.8(8)	C21	C20	C13 ¹	125.5(9)
N1	C1	C22	110.9(9)	C22	C21	C20	106.6(9)
C2	C1	C22	124.2(10)	C21	C22	C1	107.5(9)
C1	C2	C9	126.1(10)	02	P1	O3	113.4(4)
C1	C2	C3	119.6(8)	02	P1	01	114.1(4)
C9	C2	C3	114.2(10)	03	P1	01	111.5(4)
C8	C3	C4	120.1(11)	02	P1	C5	106.2(5)
C8	C3	C2	121.8(11)	03	P1	C5	105.4(5)
C4	C3	C2	117.7(8)	01	P1	C5	105.4(5)
C5	C4	C3	119.8(9)	P1	01	Zn1 ²	118.3(4)
C4	C5	C6	120.5(11)	P1	O3	Zn1 ³	157.2(4)
C4	C5	P1	120.7(7)	06	P2	O4	116.0(5)
C6	C5	P1	118.5(9)	06	P2	05	112.1(4)
C7	C6	C5	119.6(10)	04	P2	05	111.3(4)
C6	C7	C8	120.1(9)	06	P2	C18	105.9(5)
C3	C8	C7	119.6(11)	04	P2	C18	105.7(5)
N2	C9	C2	123.5(11)	05	P2	C18	104.9(5)
N2	C9	C10	109.1(8)	P2	O4	Znl	123.6(4)
C2	C9	C10	127.3(10)	P2	06	Zn1 ⁴	144.1(4)
C11	C10	C9	108.3(10)	04	Znl	O3 ³	99.4(3)
C10	C11	C12	107.7(10)	04	Zn1	O1 ⁵	98.2(3)
C13	C12	N2	124.1(11)	O3 ³	Zn1	O1 ⁵	115.4(3)
C13	C12	C11	124.9(10)	04	Znl	O6 ⁴	118.3(3)
N2	C12	C11	110.9(8)	O3 ³	Znl	O6 ⁴	97.9(3)
C12	C13	C14	116.9(10)	O1 ⁵	Znl	O6 ⁴	125.4(3)
C12	C13	$C20^1$	125.6(9)	C24	N3	C23	123.0(7)
C14	C13	$C20^1$	117.5(8)				

¹1-X,1-Y,1-Z; ²-X,1/2+Y,3/2-Z; ³-X,1-Y,1-Z; ⁴-X,-Y,1-Z; ⁵-X,-1/2+Y,3/2-Z

Table S3. Hydrogen bonds for IPCE-2Pd.

\mathbf{D}^{*}	Н	\mathbf{A}^{*}	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N3	H3A	07	0.90	1.73	2.589(9)	160
N3	H3B	$O2^1$	0.90	2.09	2.758(13)	130
05	H5	$O2^2$	0.82	1.87	2.547(8)	138
07	H7A	O1 ¹	0.91	2.06	2.926(11)	158
07	H7B	$O4^2$	0.89	1.97	2.742(8)	144

* D is a proton donor; A is a proton acceptor at the hydrogen bonds formation.

¹-X,1-Y,1-Z; ²+X,1/2-Y,-1/2+Z



Scheme S2. Model used in a search for structure solution. Torsion angles varied in simulated annealing runs are shown by arrows. The Pd–N and P–O bond lengths were fixed to 2.03 and 1.51 Å, respectively.



Figure S11. The Rietveld plot for **IPCE-2Pd** showing the experimental (black dots), calculated (blue) and difference (red) curves. The vertical green bars denote calculated positions of the diffraction peaks.



Figure S12. Coordination environment of palladium(II) porphyrinate in IPCE-2Pd.

Figure S13. Graphical representation of the coordination modes of coordinated phosphonate groups (P1-P2) of **Pd-mH₂TPPP⁶⁻** in **IPCE-2Pd**. Numbers in brackets represent the Harris notation.^[1]

Figure S14. Hydrogen bonds (donor-acceptor distances in Å) within the inorganic SBU region in the structure of IPCE-2Pd.

Figure S15. Intermolecular interactions between palladium(II) porphyrinate molecules in **IPCE-2Pd**. Phosphonate groups are omitted for clarity.

Table S4. Short contacts (Å) between adjacent palladium(II) porphyrinates in the crystal of **IPCE-2Pd**.

C6C4 ¹	3.663(13)
C7C1 ¹	3.366(14)
C7C2 ¹	3.523(13)
C7C3 ¹	3.795(13)
C7C4 ¹	3.461(14)
C7C22 ¹	3.528(14)
C8C22 ¹	3.678(13)

1+x,3/2-y,1/2+z

Topological analysis of IPCE-2Pd

The structure of **IPCE-2Pd** was simplified in ToposPro from the multidimentional system to a simple node-connected net. Two different methods were used for framework simplification: standard and cluster.

In the standard representation Zn atoms were considered as metal nodes of the framework and the porphyrin molecules as ligands. Each Zn ion is connected to four porphyrin molecules (**Figure S16a**) and each porphyrin molecule is bonded with eight Zn ions (**Figure S16b**). **IPCE-2Pd** forms 2-nodal 4,8-coordinated three-periodic net **alb-4,8-***P***2**₁*/c***-1** with point symbol $\{4^{10} \cdot 6^{14} \cdot 8^4\} \{4^5 \cdot 6\}_2$ and stoichiometry $(4-c)_2(8-c)$. Such underlying topology was found for 31 crystal structure in <u>https://topcryst.com/</u>. Among them 8 structures are valence-bonded MOFs in standard representation (e.g. ref. codes ZALREM, MAQDUD01, POPSAQ, AHEMOQ, MASZEO), the others are hydrogen-bonded molecular structures. According to a simplified nodeconnected net, the **IPCE-2Pd** framework consists of altered layers of porphyrin molecules and zinc ions as inorganic building units (**Figure S16c-f**).

Figure S16. The standard representation of **IPCE-2Pd** in ToposPro. 2-nodal 4,8-coordinated three-periodic net alb-4,8-P2₁/c-1: a) 4-connected zinc node (purple), b) 8-connected porphyrin node (blue), c) node view of simplified framework, view along [001], d) node view of simplified framework, view along [010], e) polyhedra view of simplified framework, view along [010], f) polyhedra view of simplified framework, view along [010].

In the cluster representation, the first node is the porphyrin molecule, while the second node is binuclear zinc SBU, the third node is phosphonate group (P1) which connects Zn dimers with each other. Each Zn dimer is connected to the four phosphonate groups in the monodentate mode and to two porphyrin molecules via bridging phosphonates (P2) (**Figure S17a**). Each porphyrin is connected to two Zn dimer SBUs via bridging phosphonates (P2) and to two phosphonates (P1) (**Figure S17b**). Each phosphonate is connected to one porphyrin and two different Zn dimer SBUs (**Figure S17c**). Thus, phosphonate group P1 has a different function in

the structure compared with phosphonate P2. P2 plays a role of bridging group inside the dimer SBU, while P1 connects different Zn SBUs with each other.

The topological motif of such nodes is 3-nodal 3,4,6-connected net **3,4,6T55** (Figure S17c,d) with point symbol $\{5^2 \cdot 6^2 \cdot 7 \cdot 8\}$ $\{5^2 \cdot 6\}_2$ $\{5^4 \cdot 6^4 \cdot 7^4 \cdot 8^2 \cdot 9\}$ and stoichiometry $(3-c)_2(4-c)(6-c)$. Such underlying topology was found for 15 crystal structures in <u>https://topcryst.com/</u>. Among them, 10 structures are valence-bonded MOFs in cluster representation (e.g. ref. codes FIZQAI, CAHLOO, CAHMOP, FIZPOV, CAHMEF), the others are hydrogen-bonded molecular structures. The node and polyhedral views (Figure S17d-g) clearly show the altered layers in (100) plane of nonpolar porphyrin molecules and polar phosphonate groups bound to zinc SBUs.

Figure S17. The cluster representation of **IPCE-2Pd** in ToposPro. 3-nodal 3,4,6-connected three-periodic net **3,4,6T55**: a) 6-connected binuclear zinc SBU (purple), b) 4-connected porphyrin node (blue), c) 3-connected phosphonate group P1 (yellow), d) node view of simplified framework, view along [001], e) node view of simplified framework, view along [010], f) polyhedra view of simplified framework, view along [010].

The analysis of topological analogues gives us several examples which are similar to **IPCE-2Pd**. In standard representation the most interesting examples are MASZEO^[2] and ZALREM^[3].

The morphology of IPCE-2Pd

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Figure S18. SEM images of dried sample of IPCE-2Pd with scale bar a) 200 nm, b) 1 μ m, c) 3 μ m, d) 10 μ m.

EDS data of IPCE-2Pd

Figure S19. EDS characterization of IPCE-2Pd.

Table S5. Elemental	analysis of IP	CE-2Pd based	on EDS s	pectroscopy	data in atomi	ic %.
	2			1 12		

Spectrum	C	Ν	0	Р	Zn	Pd
Spectrum 1	45.66	10.02	18.91	10.64	6.01	8.20
Spectrum 2	45.74	5.96	13.28	14.55	8.84	10.94
Spectrum 3	47.74	13.05	25.89	5.87	3.19	3.96
Spectrum 4	47.41	14.32	27.79	4.74	2.35	3.15
Spectrum 5	44.31	16.08	26.97	5.28	3.37	3.71
Spectrum 6	47.13	13.77	25.35	6.12	3.11	4.26
Spectrum 7	48.66	12.00	23.40	6.61	4.18	4.84

Figure S20. XPS spectrum of IPCE-2Pd.

Figure S21. (a) XPS spectrum of Zn2p of IPCE-2Pd. (b) XPS spectrum of Pd3d of IPCE-2Pd

Figure S22. (a) XPS spectrum of N1s of IPCE-2Pd. (b) XPS spectrum of P2p of IPCE-2Pd

Sorption properties of IPCE-2Pd

As-synthesized material of **IPCE-2Pd** 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 CO₂ adsorption–desorption isotherms were measured within the range of relative pressures from 10^{-4} to 0.995.

Figure S23. Gas adsorption–desorption isotherms of **IPCE-2Pd** for CO₂ at 195 K. Filled symbols: adsorption, open symbols: desorption.

Figure S24. Water-vapor adsorption-desorption isotherms of IPCE-2Pd at 298 K.

Figure S25. PXRD data for ICPE-2Pd before and after water adsorption measurements.

Adsorbate and temperature of	Specific s	surface area / m ² ·g ⁻¹	$V_{ m ads}/$
activation	BET	DFT	cm ³ (STP)·g ⁻¹
CO ₂ , 80 °C	12.2	6.2	6.2
CO ₂ , 100 °C	8.7	16.7	5.2
H ₂ O, 80 °C	134.2	_	61.1

Table S6. The textural parameters of IPCE-2Pd material.

TG investigations of IPCE-2Pd

Figure S26. The TGA plot of IPCE-2Pd.

Pawley-refinements of IPCE-2Pd at VT-PXRD experiments

Table S7. Monoclinic unit cell dimensions of **IPCE-2Pd** at different temperatures obtained in Pawley fitting of the powder patterns measured in $3 - 40^{\circ} 2\theta$ range on the air.

	25 °C	75 °C*	175 °C	225 °C
<i>a</i> , Å	16.755	16.765/16.028	15.987	16.054
<i>b</i> , Å	13.235	13.452/13.485	13.377	13.265
<i>c</i> , Å	11.111	11.073/11.198	11.271	11.194
β, ^o	95.63	96.04/98.26	94.78	94.47
Volume, Å ³	2452	2483/2395	2402	2377
χ^2	2.416		3.323	2.951

* The mixture of two phases – old and new ones - have been observed together.

Figure S27. The result of the Pawley fitting of **IPCE-2Pd** in TK 1200 camera (Anton Paar) in air at T=25 °C showing the experimental (black dots), calculated (blue line) and difference (red line) profiles. The vertical bars (green lines) correspond to the calculated positions of the Bragg peaks.

Structural characterization of IPCE-2Pd-HT

Atom	Atom	Length/Å	I	Atom	Atom	Length/Å
Pd1	N1	2.051(10)	(C14	C15	1.384(19)
Pd1	N1 ¹	2.051(10)	C	C14	C19	1.40(2)
Pd1	N2	2.088(13)	C	C15	C16	1.40(2)
Pd1	N2 ¹	2.088(13)	C	C16	C17	1.40(2)
N1	C1	1.38(2)	C	C17	C18	1.418(19)
N1	C20	1.387(18)	C	C18	C19	1.36(2)
N2	C9	1.407(19)	C	C18	P2	1.786(18)
N2	C12	1.407(17)	(C20	C21	1.448(19)
C1	C2	1.39(2)	(C20	C13 ¹	1.62(2)
C1	C22	1.442(18)	(C21	C22	1.33(2)
C2	C3	1.48(2)	I	P1	O3	1.491(9)
C2	C9	1.491(18)	I	P1	O2	1.522(12)
C3	C8	1.393(17)	I	P1	01	1.523(10)
C3	C4	1.41(2)	(52	Zn1 ²	1.998(8)
C4	C5	1.38(2)	(03	Zn1 ³	1.922(9)
C5	C6	1.404(17)	I	22	05	1.500(9)
C5	P1	1.790(17)	I	22	06	1.505(10)
C6	C7	1.38(2)	I	22	04	1.518(11)

Table S8. Bond lengths for IPCE-2Pd-HT.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C7	C8	1.39(2)	04	Zn1	1.865(11)
C9	C10	1.44(2)	06	Zn1 ⁴	1.850(10)
C10	C11	1.324(18)	Zn1	O6 ⁴	1.850(10)
C11	C12	1.44(2)	Zn1	O3 ³	1.922(9)
C12	C13	1.365(19)	Zn1	O2 ⁵	1.998(8)
C13	C14	1.49(2)	N3	C23	1.409(17)
C13	C20 ¹	1.62(2)	N3	C24	1.42(2)

¹1-X,1-Y,1-Z; ²-X,1/2+Y,3/2-Z; ³-X,1-Y,1-Z; ⁴-X,-Y,1-Z; ⁵-X,-1/2+Y,3/2-Z

Table S9. Bond angles for IPCE-2Pd-HT.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Pd1	N1 ¹	180.000(1)	C15	C14	C19	119.7(13)
N1	Pd1	N2	89.3(4)	C15	C14	C13	121.9(14)
$N1^1$	Pd1	N2	90.7(4)	C19	C14	C13	118.3(12)
N1	Pd1	N2 ¹	90.7(4)	C14	C15	C16	120.1(15)
$N1^1$	Pd1	N2 ¹	89.3(4)	C15	C16	C17	120.7(13)
N2	Pd1	N2 ¹	180.000(1)	C16	C17	C18	117.3(13)
C1	N1	C20	104.4(11)	C19	C18	C17	121.8(15)
C1	N1	Pd1	128.3(9)	C19	C18	P2	129.1(12)
C20	N1	Pd1	126.3(10)	C17	C18	P2	108.7(11)
С9	N2	C12	104.1(12)	C18	C19	C14	120.1(13)
C9	N2	Pd1	127.0(9)	N1	C20	C21	110.3(14)
C12	N2	Pd1	128.9(9)	N1	C20	C13 ¹	125.0(11)
N1	C1	C2	125.9(12)	C21	C20	C13 ¹	123.1(12)
N1	C1	C22	110.5(13)	C22	C21	C20	107.1(12)
C2	C1	C22	123.4(14)	C21	C22	C1	107.5(13)
C1	C2	C3	120.4(12)	O3	P1	O2	112.8(6)
C1	C2	C9	125.1(14)	O3	P1	01	112.8(5)
C3	C2	C9	114.5(14)	O2	P1	01	111.2(6)
C8	C3	C4	119.0(14)	O3	P1	C5	108.1(7)
C8	C3	C2	119.5(14)	O2	P1	C5	105.7(6)
C4	C3	C2	120.7(11)	01	P1	C5	105.6(6)
C5	C4	C3	120.4(11)	P1	O2	Zn1 ²	122.9(6)
C4	C5	C6	119.6(15)	P1	O3	Zn1 ³	124.7(6)
C4	C5	P1	123.2(10)	05	P2	O6	113.1(5)
C6	C5	P1	117.1(12)	05	P2	O4	112.9(6)
C7	C6	C5	120.2(14)	06	P2	O4	111.8(6)
C6	C7	C8	120.0(12)	05	P2	C18	107.9(7)
C7	C8	C3	120.2(14)	06	P2	C18	107.3(7)
N2	C9	C10	109.5(11)	O4	P2	C18	103.1(6)
N2	C9	C2	123.5(14)	P2	O4	Zn1	136.3(6)
C10	C9	C2	127.0(14)	P2	O6	Zn1 ⁴	139.9(7)
C11	C10	C9	108.7(14)	O6 ⁴	Zn1	O4	106.7(4)
C10	C11	C12	107.4(13)	O6 ⁴	Zn1	O3 ³	110.2(4)
C13	C12	N2	125.5(15)	O4	Znl	O3 ³	108.5(5)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	C12	C11	124.3(13)	O6 ⁴	Zn1	O2 ⁵	111.5(4)
N2	C12	C11	110.2(12)	04	Zn1	O2 ⁵	90.0(4)
C12	C13	C14	119.1(15)	O3 ³	Zn1	O2 ⁵	126.4(4)
C12	C13	C20 ¹	121.0(12)	C23	N3	C24	126.5(11)
C14	C13	C20 ¹	118.5(11)				

 $^{1}1\text{-}X, 1\text{-}Y, 1\text{-}Z; \ ^{2}\text{-}X, 1/2 + Y, 3/2 \text{-}Z; \ ^{3}\text{-}X, 1\text{-}Y, 1\text{-}Z; \ ^{4}\text{-}X, \text{-}Y, 1\text{-}Z; \ ^{5}\text{-}X, \text{-}1/2 + Y, 3/2 \text{-}Z$

Table S10. Hydrogen bonds for IPCE-2Pd-HT.

\mathbf{D}^*	Н	\mathbf{A}^{*}	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N3	H3A	011	0.90	2.31	3.132(14)	151
N3	H3B	$O2^2$	0.90	2.14	3.021(16)	165
05	H5	O1 ²	0.82	1.78	2.398(16)	131

* D is a proton donor; A is a proton acceptor at the hydrogen bonds formation.

¹+X,3/2-Y,-1/2+Z; ²-X,1-Y,1-Z

Figure S28. The Rietveld plot for **IPCE-2Pd-HT** showing the experimental (black dots), calculated (blue) and difference (red) curves. The vertical green bars denote calculated positions of the diffraction peaks

Figure S29. Hydrogen bond (donor-acceptor distances in Å) within the inorganic SBU region in the structure of **IPCE-2Pd-HT**.

Figure S30. The result of the Pawley fitting of **IPCE-2Pd** in TK 1200 camera (Anton Paar) in air at T=175 °C showing the experimental (black dots), calculated (blue line) and difference (red line) profiles. The vertical bars (green lines) correspond to the calculated positions of the Bragg peaks

Figure S31. The result of the Pawley fitting of **IPCE-2Pd** in TK 1200 camera (Anton Paar) in air at T=225 °C showing the experimental (black dots), calculated (blue line) and difference (red line) profiles. The vertical bars (green lines) correspond to the calculated positions of the Bragg peaks.

Figure S32. PXRD data for sample of **ICPE-2Pd** heated at 175 °C before and after immersion in water for 7 days.

Figure S33. PXRD data for sample of **ICPE-2Pd** heated at 225 °C before and after immersion in water for 7 days.

PXRD patterns of IPCE-2Pd immersed in various solvents

Pawley-refinements of IPCE-2Pd immersed in various solvents

For all samples of **IPCE-2Pd** immersed in various solvents, the monoclinic unit cell dimensions and space group $P2_{1/c}$ were tested in Pawley fits^[4] with the program *MRIA*^[5]. The unit cell dimensions and $\chi 2$ values are shown in **Table S11**.

	Dry	HEX	Acetone	CH ₂ Cl ₂	CHCl ₃	THF	MeOH	EtOH	H ₂ O
<i>a</i> , Å	16.713	16.688	16.697	16.692	16.692	16.701	16.682	16.680	16.698
b, Å	13.407	13.380	13.392	13.386	13.390	13.395	13.307	13.330	13.253
<i>c</i> , Å	11.130	11.108	11.134	11.133	11.124	11.134	11.145	11.106	11.154
β, ^o	95.92	95.98	95.94	95.94	95.97	95.97	96.03	96.03	96.02
Volume, Å ³	2481	2467	2476	2474	2473	2477	2460	2456	2455
χ^2	1.875	1.477	1.279	1.339	1.465	1.436	1.441	1.063	

Table S11. Monoclinic unit cell dimensions and $\chi 2$ values of **IPCE-2Pd** immersed in different solvents obtained in Pawley fitting of the powder patterns measured in $3 - 40^{\circ} 2\theta$ range.

In view of closeness of all patterns herewith we present only three of them, namely, THF with the best crystallinity on **Figure S35** and EtOH and water with the worst crystallinity on **Figure S36-Figure S37**.

Figure S35. The result of the Pawley fitting of **IPCE-2Pd** kept in THF showing the experimental (black dots), calculated (blue line) and difference (red line) profiles. The vertical bars (green lines) correspond to the calculated positions of the Bragg peaks.

Figure S36. The result of the Pawley fitting of **IPCE-2Pd** kept in ethanol showing the experimental (black dots), calculated (blue line) and difference (red line) profiles. The vertical bars (green lines) correspond to the calculated positions of the Bragg peaks.

Figure S37. The result of the Pawley fitting of **IPCE-2Pd** kept in water showing the experimental (black dots), calculated (blue line) and difference (red line) profiles. The vertical bars (green lines) correspond to the calculated positions of the Bragg peaks.

Figure S38. Nyquist plots of IPCE-2Pd at 85% RH and different temperatures.

Figure S39. Nyquist plots of IPCE-2Pd at 95% RH and different temperatures.

Figure S40. PXRD data for ICPE-2Pd before and after proton conductivity measurements.

Figure S41. PXRD data for **IPCE-2Pd** before and after reflux in water for 7 days, where one can see good coincidence of peak positions in both powder patterns, i.e unit cell parameters and space groups in both samples are identical (see also **Figure S42** below). The difference in the heights of peaks in both patterns is caused by the strong preferred orientation effect in the refluxed sample.

Figure S42. The result of the Pawley fitting of **IPCE-2Pd** after reflux in water for 7 days showing the experimental (black dots), calculated (blue line) and difference (red line) profiles. The vertical bars (green lines) correspond to the calculated positions of the Bragg peaks. The obtained values of monoclinic unit cell dimensions are: a = 16.747 Å, b = 13.362 Å, c = 11.131 Å, $\beta = 95.98^{\circ}$, volume = 2477 Å³ – compare with those in **Table S11**.

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