Electronic Supplementary Information

Synthesis and Electrochemical properties of metal(II)-carboxyethylphenylphosphinates

Montse Bazaga-García,[a] Álvaro Vílchez-Cózar,[a] Bianca Maranescu,[b] P. Olivera-Pastor,[a] Marko Marganovici,[c] Gheorghe Ilia,[b,c] Aurelio Cabeza Díaz,[a] Aurelia Visa*[b] and Rosario M. P. Colodrero*[a]

[a]*Dpo Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos s/n, 29071-Málaga, Spain*
[b]*"Coriolan Dragulescu" Institute of Chemistry, 24 Mihai Viteazu Bvd. 300223-Timisoara, Romania*
[c]*West University Timisoara, Faculty of Chemistry, Biology, Geography, Dept. of Biology-Chemistry, 16 Pestalozzi Street, 300115, Timisoara, Romania*

Table of contents:

Figures:

Tables:

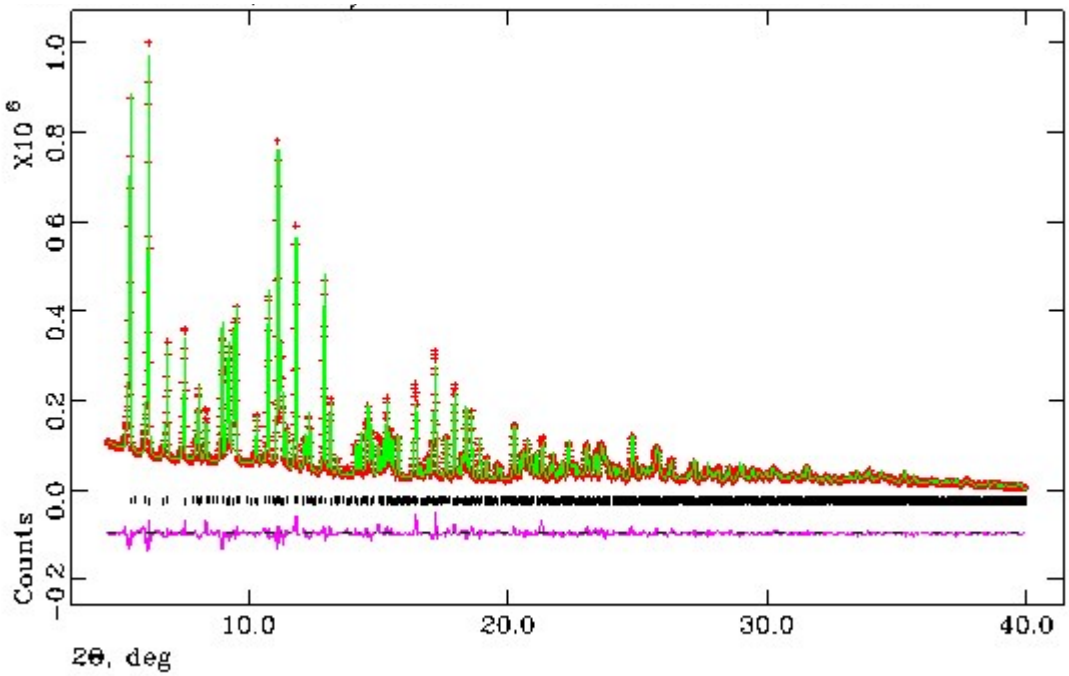

Fig. S1 Final Rietveld plot for **Cd[$O_2P(CH_2CH_2COOH)(C_6H_5)$]$_2$ (1).**

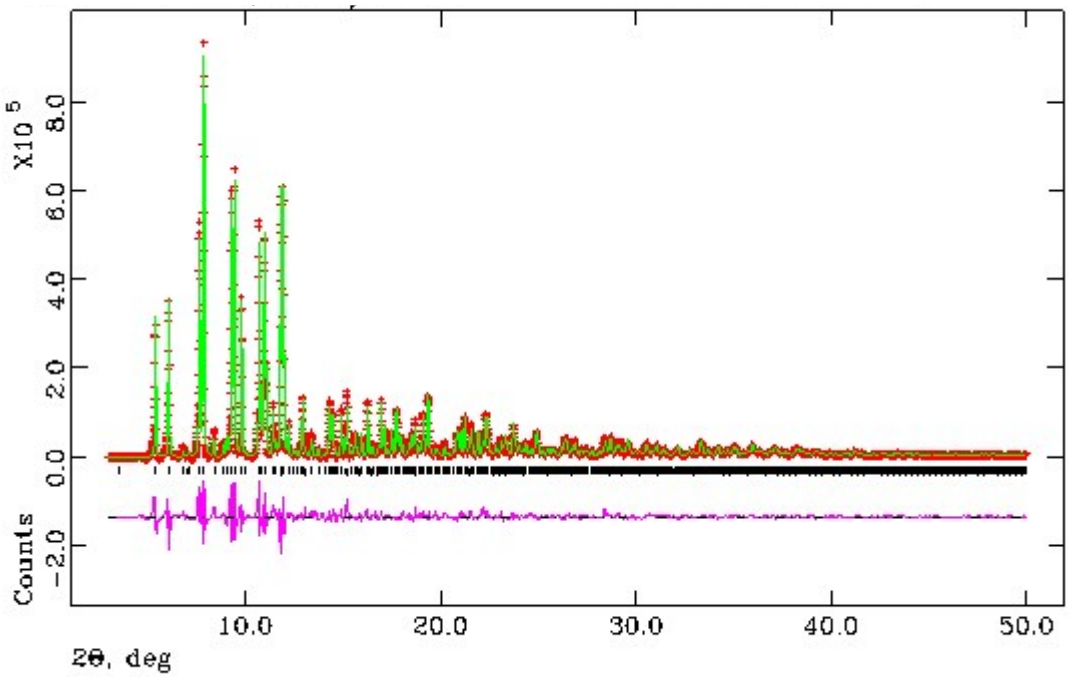

Fig. S2 Final Rietveld plot for **Ca[$O_2P(CH_2CH_2COOH)(C_6H_5)$]$_2$ (2)**.

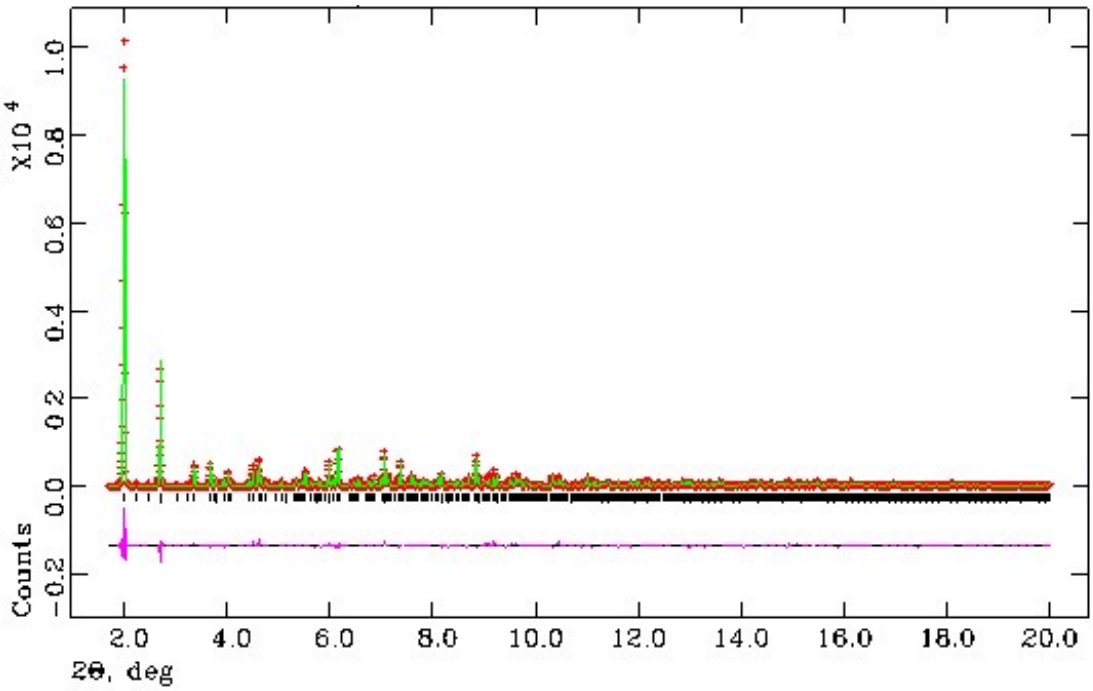

Fig. S3 Final Rietveld plot for **$Co_2[(O_2P(CH_2CH_2COO)(C_6H_5)(H_2O)]_2 \cdot 2H_2O$ (3)**.

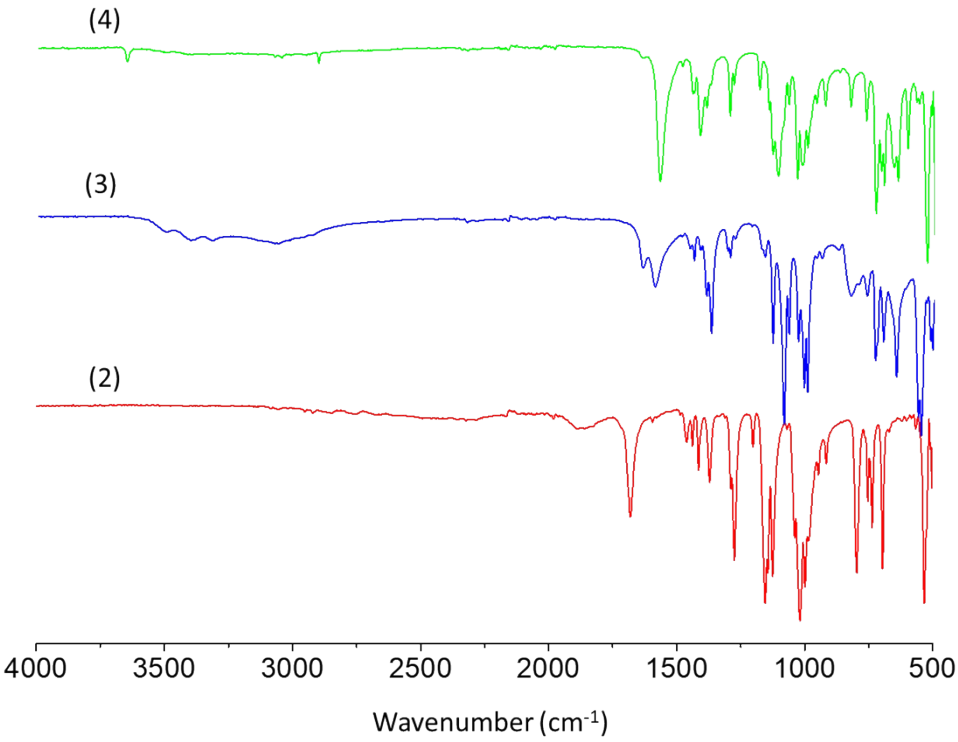

Fig. S4 FT-IR spectra of: (a) **$Co_3(O_2P(CH_2CH_2COO)(C_6H_5))_2(OH)_2$ (4)**, (b) **$Co_2[(O_2P(CH_2CH_2COO)(C_6H_5)(H_2O)]_2 \cdot 2H_2O$ (3)** and (c) **$Ca[O_2P(CH_2CH_2COOH)(C_6H_5)]_2$ (2)**.

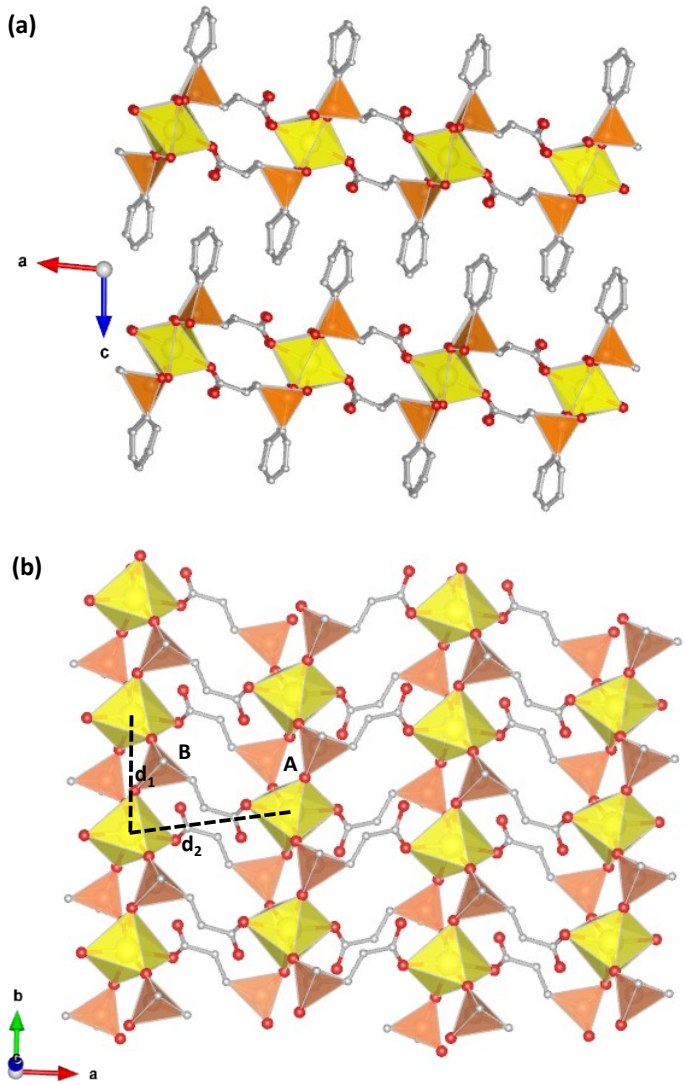

Fig. S5 (a) Layered packing of **$Cd[O_2P(CH_2CH_2COOH)(C_6H_5)]_2$ (1)** and (b) details of a hybrid layer in **$Cd[O_2P(CH_2CH_2COOH)(C_6H_5)]_2$ (1)** showing the 8-member rings (A) and 14-member rings (B)**.**

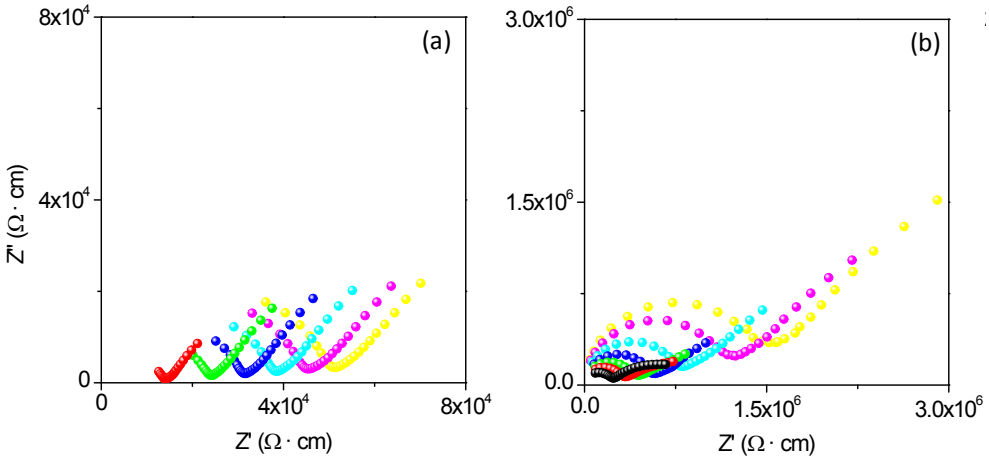

Fig. S6 Plots of the complex impedance plane for (a) **CEPPA ligand** and (b) **$Co_2[(O_2P(CH_2CH_2COO)(C_6H_5)(H_2O)]_2 \cdot 2H_2O$ (3)** at 95 %RH and various temperatures: 80 (black), 70 (red), 60 (green), 50 (blue), 40 (cyan), 30 (magenta) and 25 °C (yellow).

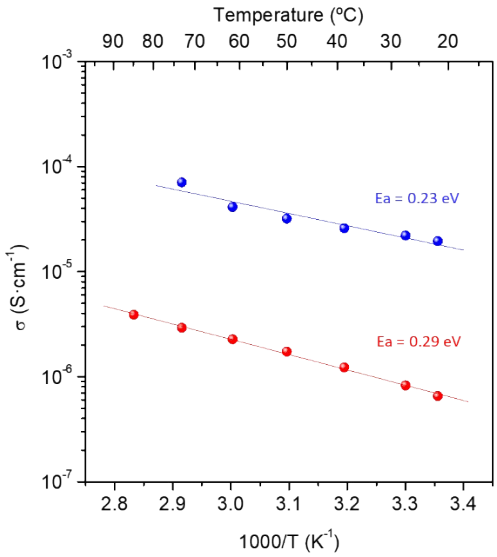

Fig. S7 Arrhenius plots for **$Co_2[(O_2P(CH_2CH_2COO)(C_6H_5)(H_2O)]_2 \cdot 2H_2O$ (3)** (red) and **CEPPA ligand** (blue) at 95 % RH and different temperatures.

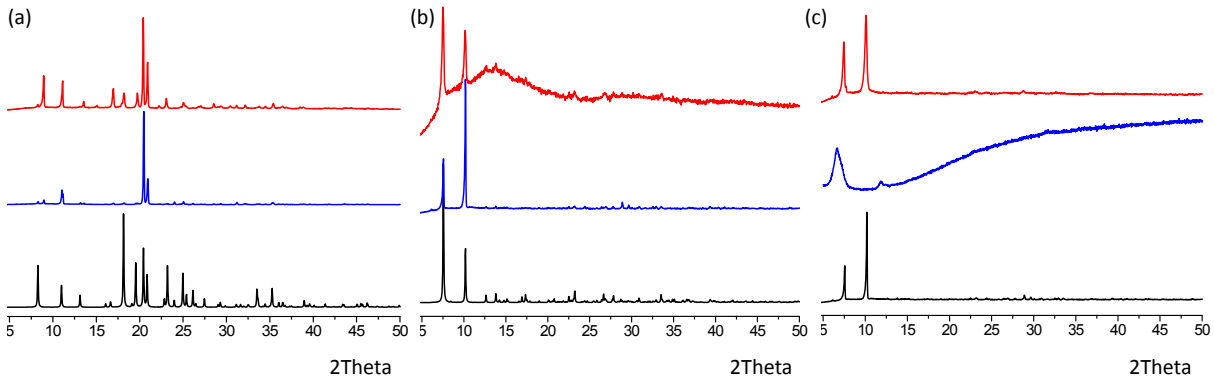

Fig. S8 Comparative of XRPD patterns for (a) **CEPPA** ligand, and (b) **$Co_2[(O_2P(CH_2CH_2COO)(C_6H_5)(H_2O)]_2 \cdot 2H_2O$ (3)** samples, simulated XRPD (black), as synthetized (blue) and after (red) proton conductivity measurements. (c) XRPD patterns for **3**: as synthetized (black), anhydrous at 200 °C (blue) and rehydrated at 95% RH (red).

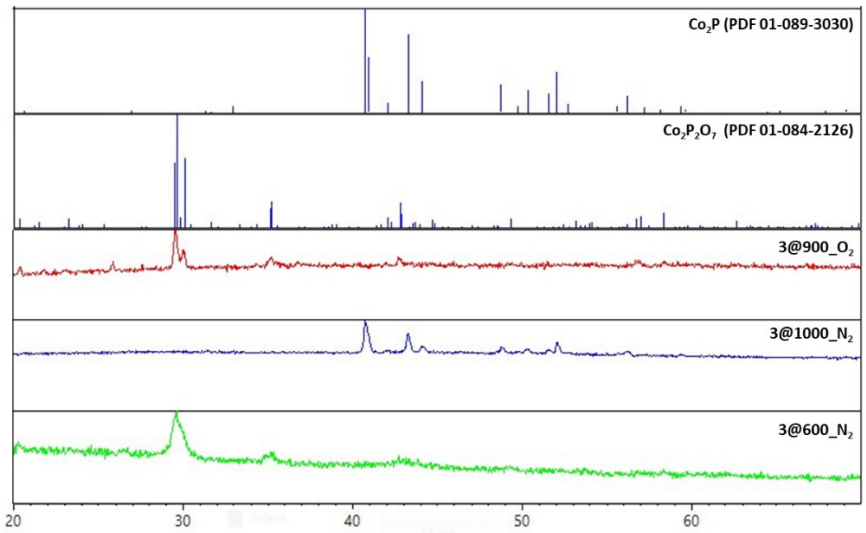

Fig. S9 PXRD patterns of the **$Co_2[(O_2P(CH_2CH_2COO)(C_6H_5)(H_2O)]_2 \cdot 2H_2O$ (3)** pyrolyzed at different temperatures and atmospheres.

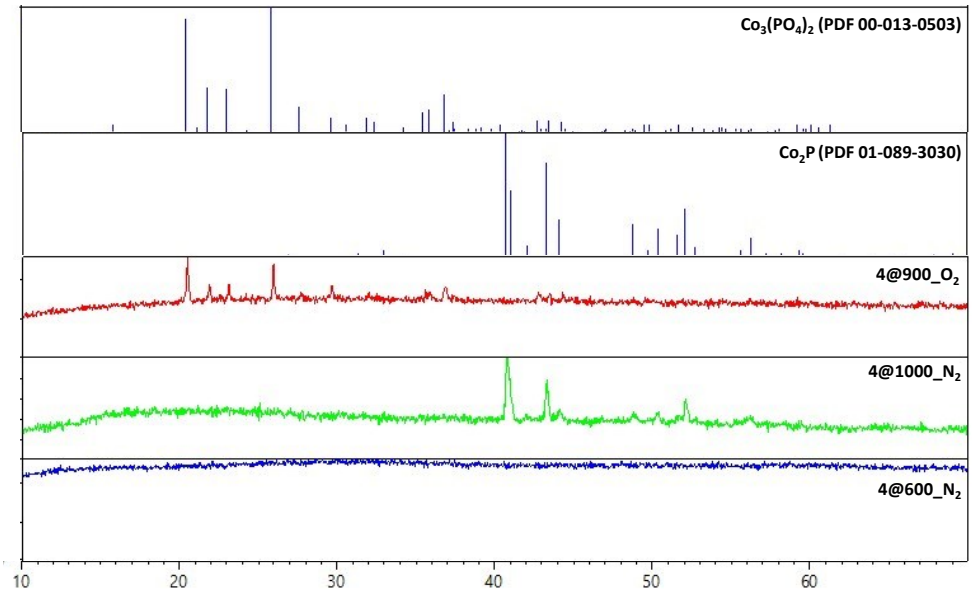

Fig. S10 PXRD patterns of the **$Co_3(O_2P(CH_2CH_2COO)(C_6H_5))_2(OH)_2$ (4)** pyrolyzed at different temperatures and atmospheres.

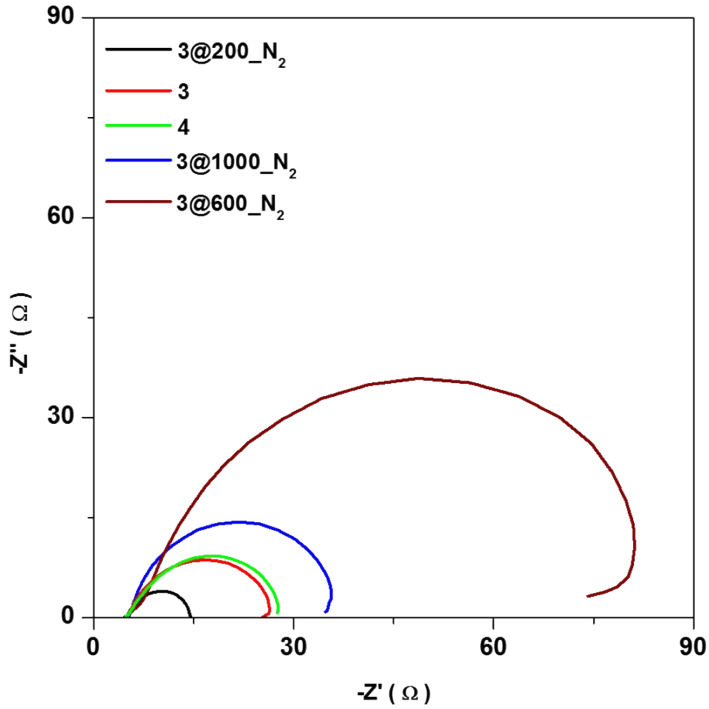

Fig. S11 Nyquist plots for selected cobalt(II) phosphinates and selected calcinated derivatives.

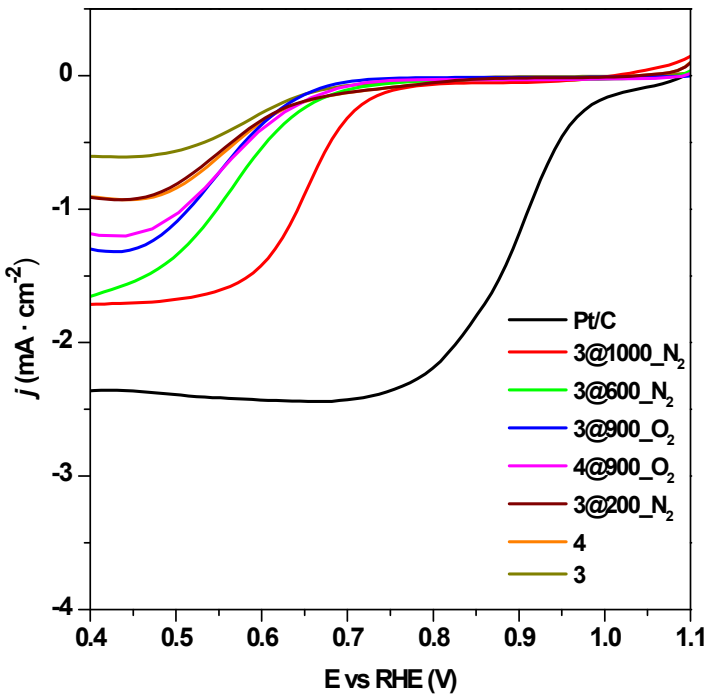

Fig. S12 LSV curves of cobalt(II) phosphinates and their pyrolytic derivatives for the oxygen reduction reaction (ORR).

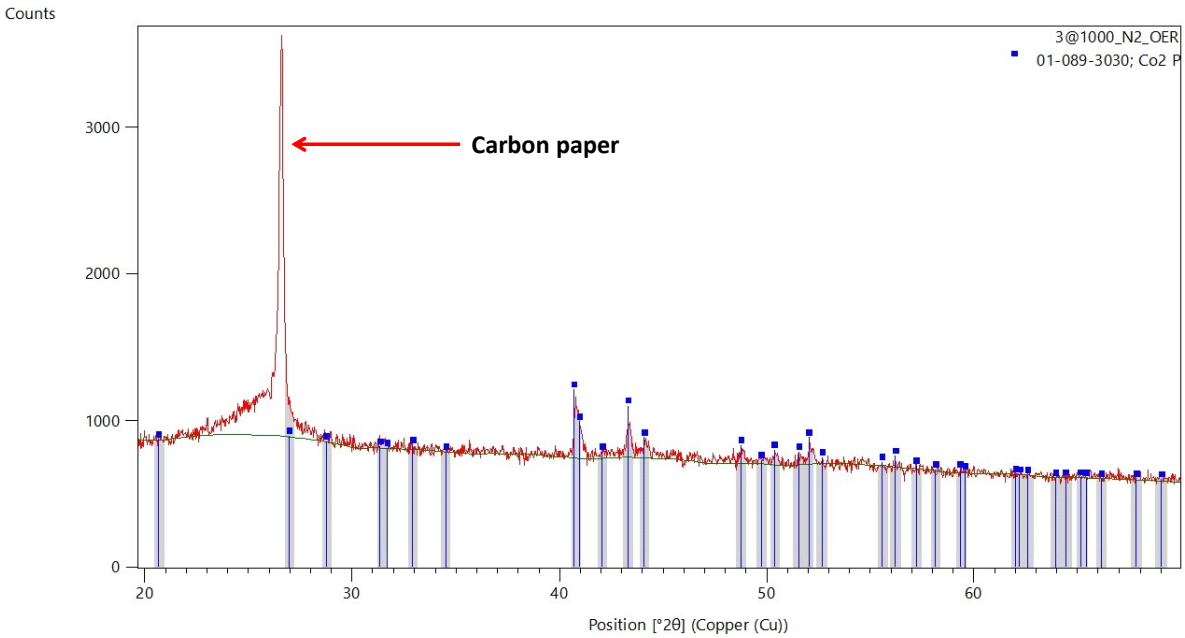

Fig. S13 PXRD pattern of **3@1000C_N_2** after OER test

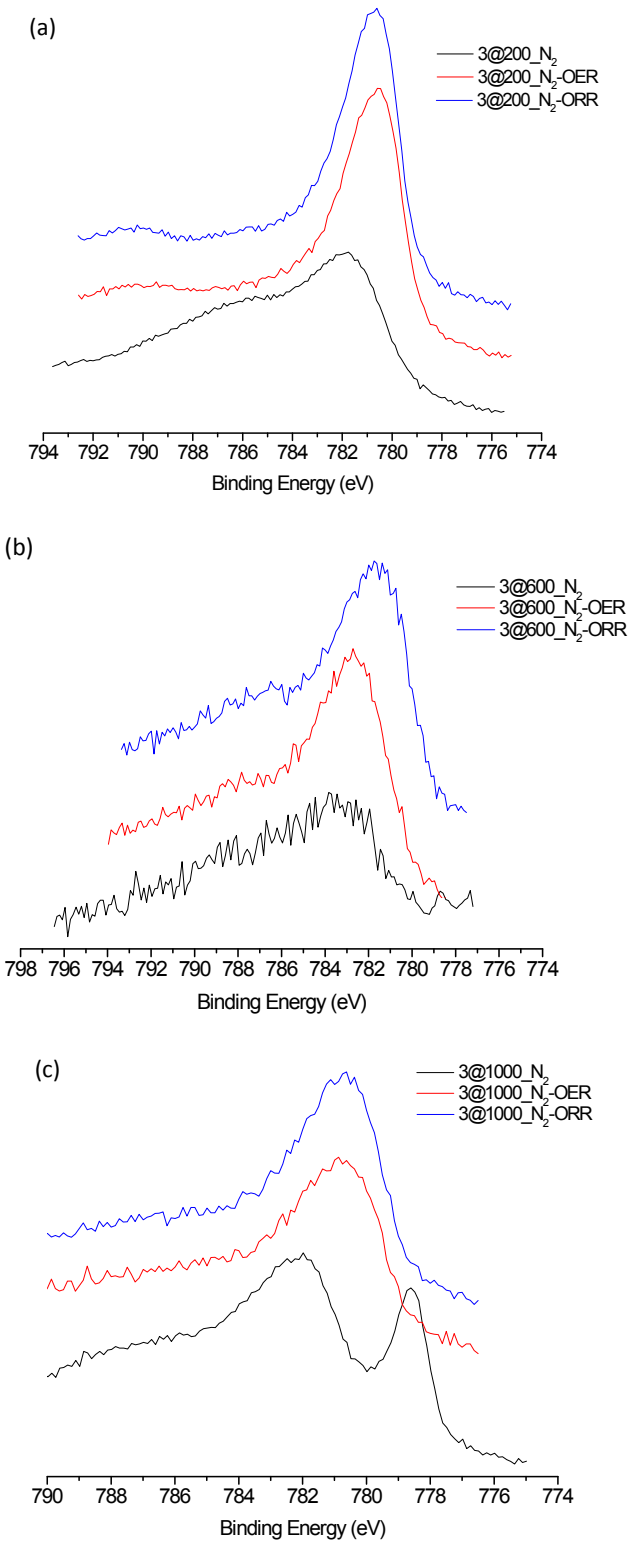

Fig. S14 XPS for Co $2p_{3/2}$ region of pyrolyzed derivative of compound **3**, before (black line) and after OER (red line) and ORR (blue line) tests**.**

Table S1. Selected bond lengths (Å) for compounds **1** – **3**.

Sample	Bond	Length	Bond	Length
1	Cd1 – O1	2.138(12)	P1 – O1	1.530(8)
	Cd1 – O2	2.282(13)	P1 – O2	1.521(8)
	Cd1 – O4	2.336(14)	P1 – C1	1.815(7)
	Cd1 – O5	2.149(12)	P1 – C7	1.811(8)
	Cd1 – O6	2.276(13)		
	Cd1 – O7	2.326(14)		
2	Ca1 – O1	2.573(18)	P1 – O1	1.530(8)
	Ca1 – O2	2.262(14)	P1 – O2	1.529(8)
	Ca1 – O4	2.506(25)	P1 – C1	1.822(7)
	Ca1 – O5	2.286(16)	P1 – C7	1.799(8)
	Ca1 – O6	2.250(14)		
	Ca1 – O7	2.540(24)		
3	Co1 – O11 x 2	2.434(16)	P1 – O11	1.533(11)
	Co1 – O41 x 2	2.270(16)	P1 – O21	1.515(11)
	Co1 – O12 x 2	2.224(16)	P1 – C11	1.836(13)
	Co2 – O21 x 2	2.164(15)	P1 – C41b	1.824(11)
	Co2 – O22 x 2	2.404(15)		
	Co2 – O32 x 2	2.294(16)	P2 – O12	1.580(11)
	Co3 – O11	2.061(15)	P2 – O22	1.513(11)
	Co3 – O41	2.277(17)	P2 – C12	1.805(12)
	Co3 – O22	2.069(15)	P2 – C42b	1.809(11)
	Co3 – O32	2.247(16)		
	Co3 – Ow1	2.025(19)		
	Co3 – Ow2	2.143(16)		

Table S2. H-bond distances for **$Co_2[(O_2P(CH_2CH_2COO)(C_6H_5)(H_2O)]_2 \cdot 2H_2O$ (3)**.

D-H···A	D···A (Å)	D-H···A	D···A (Å)
Ow1···O42	2.613(63)	Ow2···Ow3	2.725(23)
Ow1···Ow4	2.667(23)	Ow3···O21	2.802(24)
Ow1···Ow4	2.682(24)	Ow3···O42	2.715(23)
Ow1···O11	2.948(25)	Ow4···O31	2.751(26)
Ow1···Ow2	2.700(22)	Ow4···O31	2.751(26)
Ow2···O31	2.599(23)	Ow4···O12	2.696(22)

Table S3. XPS data for compound **3** and its pyrolyzed derivatives before and after OER and ORR tests

Sample	B.E. (eV)	Surface Atomic Concentration (%)		
	$Co2p_{3/2}$	Co	P	Co/P
3	781.37	7.22	5.69	1.27
3-OER	780.01	6.47	0.63	10.27
3-ORR	780.36	8.70	0.38	22.89
3@200_N_2-OER	780.34	4.32	0.39	11.07
3@200_N_2-ORR	780.49	4.13	0.18	22.94
3@600_N_2	781.79	0.74	0.67	1.10
3@600_N_2-OER	781.79	2.51	1.48	1.69
3@600_N_2-ORR	781.16	1.78	0.87	2.04
3@1000_N_2	781.72	5.02	5.85	0.86
3@1000_N_2-OER	780.72	2.27	0.90	2.52
3@1000_N_2-ORR	780.74	1.85	0.63	2.93