Supplementary Information for:

Mixed-ligand Co metal-organic framework and its carbon composites as excellent electrocatalysts for oxygen evolution reaction in green-energy devices

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Experimental Section

The dipyridyl functionalised BODIPY ligand was synthesized according to the method we reported previously.[1] All other reagents and solvents were commercially available and used without further purification. The ^{1}H-NMR spectra were recorded on an Agilent 400-MR spectrometer using the residual protonated solvent as an internal standard. Thermal properties were studied using a Perkin-Elmer Instrument system (STA6000) at a heating rate of 10 °C/min under a dinitrogen atmosphere and a flow rate of 20 mL/min. Powder XRD was recorded on Rigaku SmartLab X-ray diffractometer. Gas sorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 surface area analyzer with prior degassing at 80 °C for 12 h.

Electrochemical measurements:

The activity of the prepared CoBDPMOF/Carbon materials for OER electrocatalysis was assessed using a three-electrode system with a saturated calomel electrode (SCE) as the reference electrode, a platinum coil as the counter electrode, and the CoBDPMOF/Carbon as the working electrode. A graphite reference electrode was used during stability experiments. All electrochemical measurements were performed at room temperature (25 °C) using an ALS/DY2325 Bi-Potentiostat from ALS-Japan. All potentials have been converted (and presented) to the reference hydrogen electrode (RHE) scale using the equation E(RHE) = E(SCE) + 0.242 + 0.059pH. Electrodes were placed in 1 M KOH (80 mL, Sigma-Aldrich, Taufkirchen, Germany) as supporting electrolyte.

Electrochemical characterization and investigation of the catalytic activity of the samples were performed using standard electrochemical methods: cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and chronoamperometry. The capacitance measurements were done in a deaerated solution achieved by bubbling nitrogen (Air Liquide, 99.998 vol.%) into the electrolyte solution for 20 min before the experiments and keeping a gentle flow of N_2 just above the electrolyte while running the measurements. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 100 kHz to 0.1 Hz at 1.67 V vs RHE. For OER studies, 5 LSVs were run in OER polarization conditions at a scan rate of 10 mV s^{-1}. The stability test was run in chronoamperometric mode at a constant potential of 1.7 V for 24 h.

X-Ray Structure Determination

A crystal of **CoBDPMOF** was mounted on a loop and reflection data was collected using a Bruker APEX-II CCD-based diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The hemisphere of the reflection data was collected as φ and ω scan frames at 0.5 o/frame and an exposure time of 10 s/frame. The cell parameters were determined and refined by the SMART APEX2 program.[2] Data reduction was performed using the SAINT software. The data were corrected for Lorentz and polarization effects. Empirical absorption correction was applied using the SADABS program.[3] The structures of the compounds were obtained by direct methods and refined by full-matrix least-squares methods using the SHELXTL program package [4] and Olex 2 program [5] with anisotropic thermal parameters for all non-hydrogen atoms. In view of instability in refinement, several restrains were included. All hydrogen atoms bonded to carbon were included in the model at geometrically calculated positions and refined using a riding model. The hydrogen atoms of the crystallization water molecule were located in the difference Fourier synthesis and refined with the help of distance restraints; hydrogen atoms for the remaining water molecule (O27) could not be located. Crystallographic details are summarized in Table S1. Figures of molecular structures were drawn with MERCURY program. **CCDC No. 2250942** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].
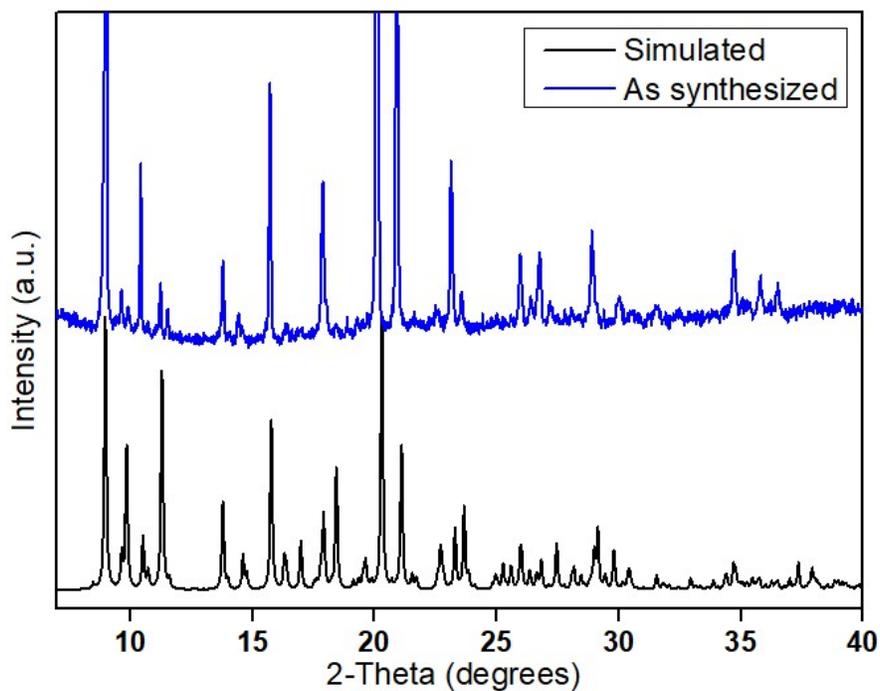
Figure S1: Powder XRD pattern of simulated and as synthesized **CoBDPMOF**.
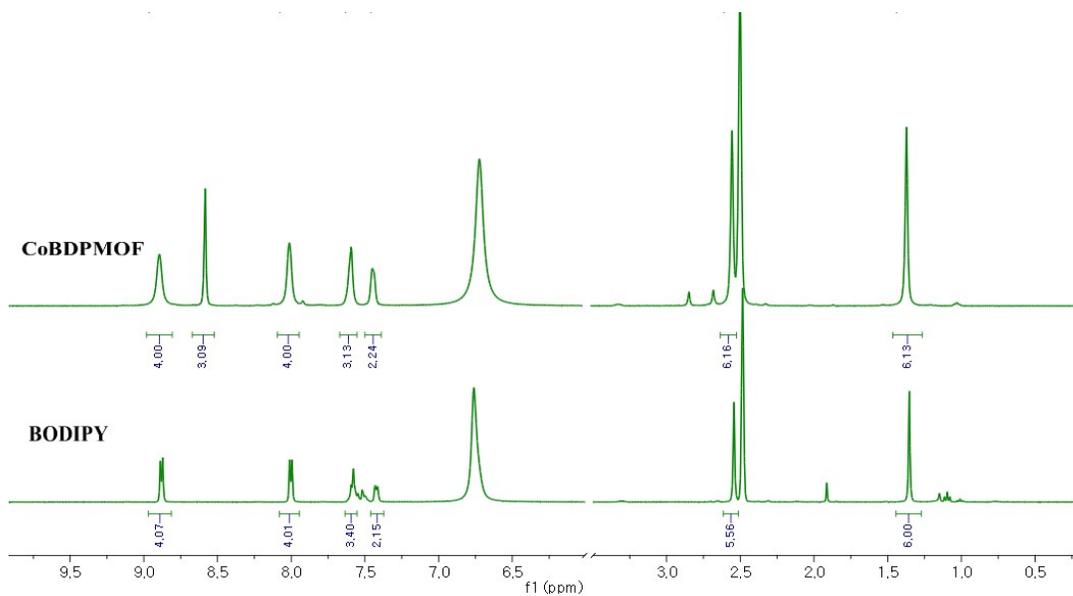
Figure S2: ^{1}H NMR spectra of the digested **CoBDPMOF** and of the functionalized BODIPY moiety in DCl/DMSO-d6 (1:9) solution; resonances pertaining to each ligand types are clear.
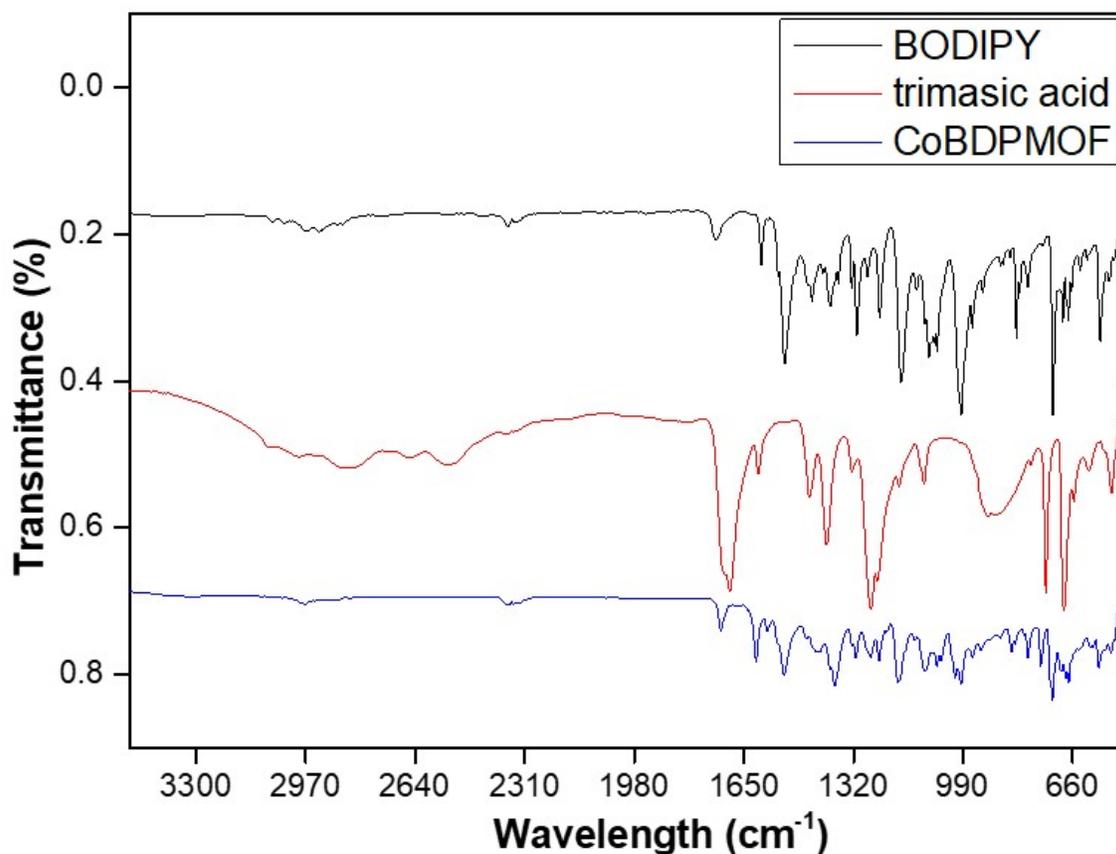
Figure S3: Infrared spectra of the free BODIPY ligand, trimasic acid and **CoBDPMOF**.
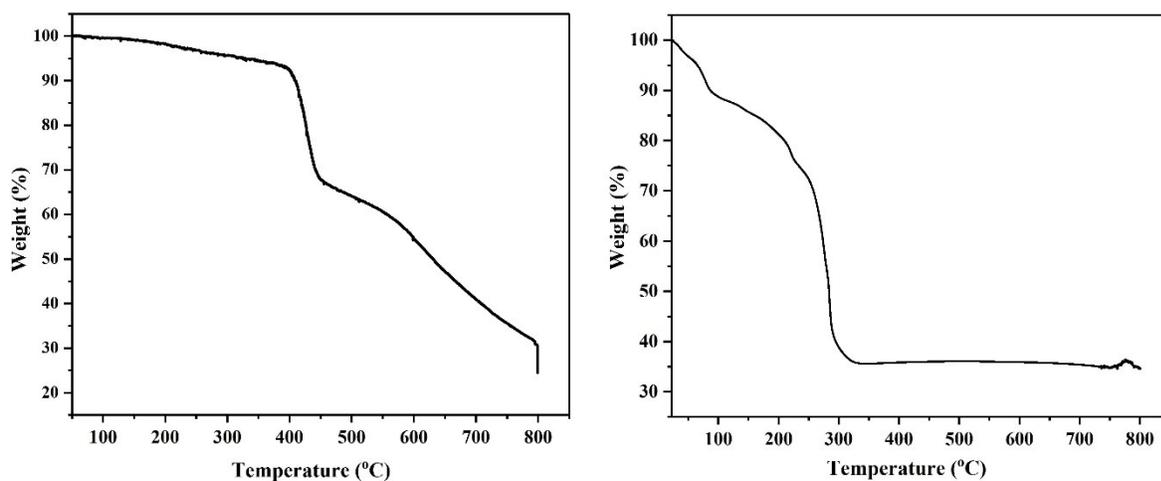
Figure S4: TGA analysis of **CoBDPMOF** (left) and **CoBTC** (right).

(a)

(b)
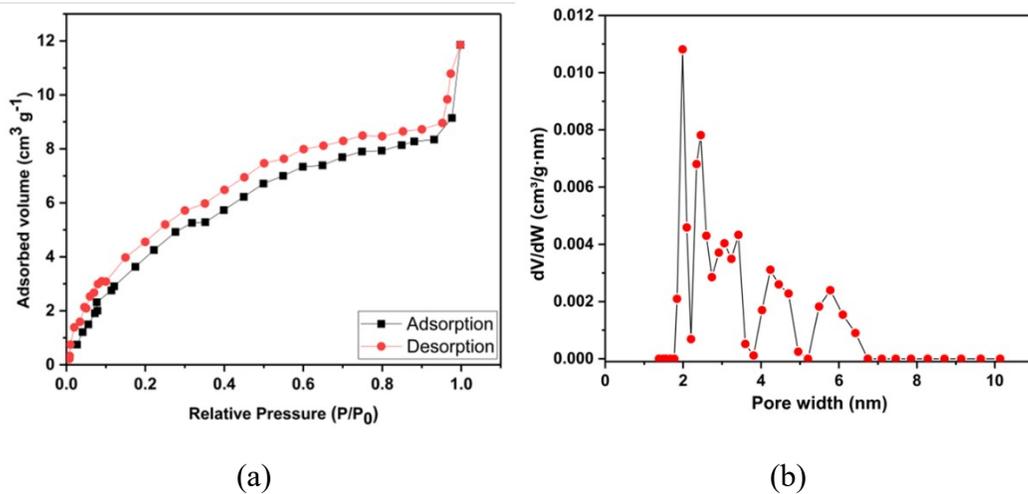
Figure S5. N$_2$ adsorption isotherms at 77 K for the **CoBDPMOF** (a) and its NLDFT PSD (b).

(a)

(b)
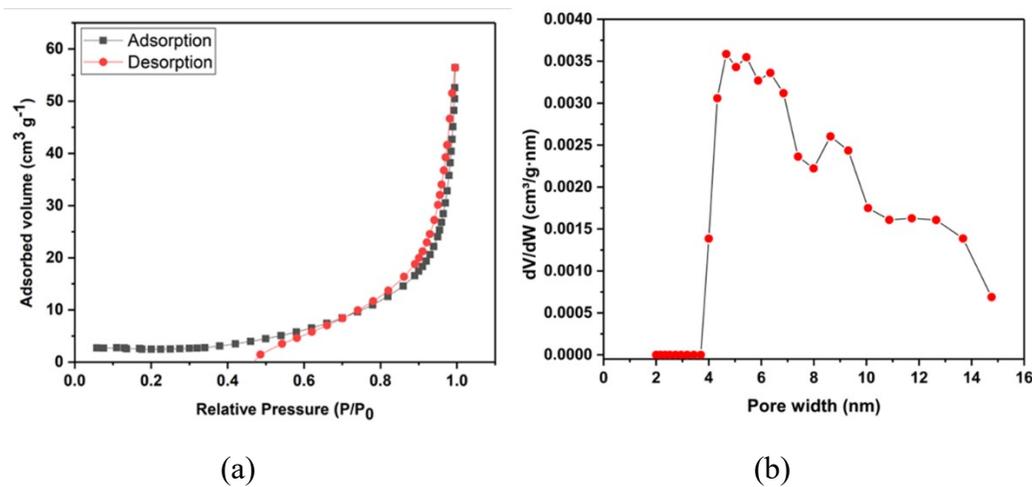
Figure S6. N$_2$ adsorption isotherms at 77 K for the **CoBTC** (a) and its NLDFT PSD (b).
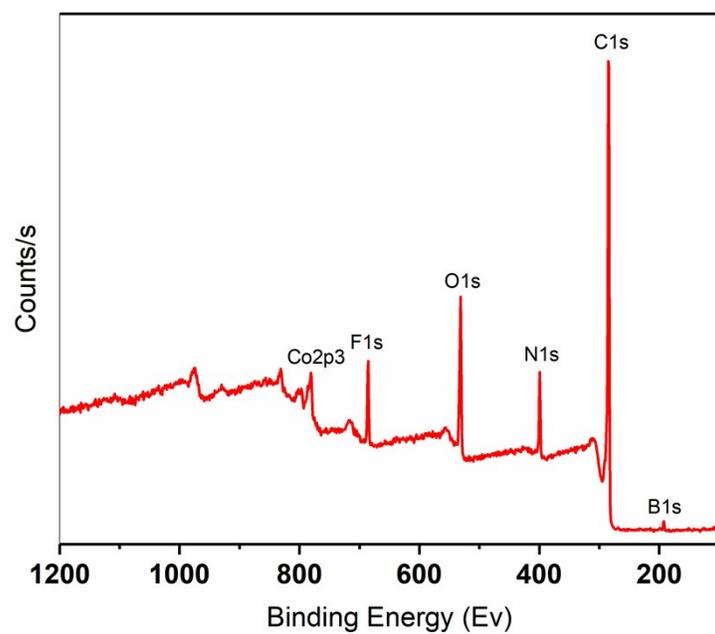
Figure S7: XPS survey spectrum of **CoBDPMOF**.

| Electron Image 3 | C K series | N K series |
| O K series | F K series | Co K series |

Element	Line Type	Apparent Concentration	k Ratio	Wt %
C	K series	8.15	0.08146	**61.47**
N	K series	0.51	0.00092	**3.60**
O	K series	1.96	0.00660	**12.86**
F	K series	5.50	0.01081	**15.84**
Co	K series	1.47	0.01469	**6.23**
Total:				100.00

(a)

Element	Line Type	Apparent Concentration	k Ratio	Wt %
C	K series	6.38	0.06382	61.57
N	K series	0.25	0.00045	2.19
O	K series	1.48	0.00497	11.68
F	K series	5.07	0.00995	17.28
Co	K series	1.39	0.01389	7.28
Total:				100.00

(b)

Figure S8: Elemental mapping and EDX analysis of CoBDPMOF (a) and CoBDPMOF@AC (b).

Element	Line Type	Apparent Concentration	k Ratio	Wt %
C	K series	9.11	0.09114	61.70
N	K series	0.54	0.00097	3.44
O	K series	2.08	0.00699	12.27
F	K series	6.54	0.01285	16.74
Co	K series	1.53	0.01531	5.85
Total:				100.00

(a)

Element	Line Type	Apparent Concentration	k Ratio	Wt %
C	K series	6.31	0.06311	60.71
N	K series	0.19	0.00034	1.59
O	K series	1.36	0.00459	10.18
F	K series	6.31	0.01239	19.82
Co	K series	1.52	0.01519	7.70
Total:				100.00

(b)

Figure S9: Elemental mapping and EDX analysis of **CoBDPMOF@CNT** (a) and **CoBDPMOF@rGO** (b).

Figure S10: Capacitance plots of **CoBDPMOF@AC** (A) and the difference between cathodic and anodic current density vs. scan rate for the studied materials (B-E).

Table S1. Crystal data and structure refinement for **CoBDPMOF.**

	CoBDPMOF
CCDC #	2250942
Empirical formula	$C_{38}H_{31}B_1Co_1F_2N_4O_7$
Formula weight	763.41
Temperature/K	100
Crystal system	triclinic
Space group	$P\bar{1}(2)$
a/Å	10.3351(4)
b/Å	10.7704(4)
c/Å	15.9693(5)
α/°	91.472(2)
β/°	100.354(2)
γ/°	103.714(2)
Volume/Å³	1694.45(11)
Z	2
$\rho_{calc}g/cm^3$	1.496
μ/mm^{-1}	0.576
F(000)	786
Reflections collected	16829
Independent reflections	3916
R_{int}	0.815
Reflections with I > 2σ(I)	6076
Restraints/Parameters	0/486
Goodness-of-fit on F2	1.011
Final R indexes [I>=2σ (I)]	0.0628
Final R indexes [all data]	0.1227
Largest diff. peak/hole / e Å⁻³	0.898/−0.670

[a] $R_1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR_2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$.

References:

[1] G. Gupta, A. Das, K. C. Park, A. Tron, H. Kim, J. Mun, N. Mandal, K.-W. Chi and C. Y. Lee, *Inorg. Chem*., 2017, **56**, 4615-4621.

[2] Bruker-AXS (2014). APEX2. Version 2014.11-0. Madison, Wisconsin, USA.

[3] L. Krause, R. Herbst-Irmer, G. M. Seldrick and D. Stalke, *J. Appl. Crystallogr*., 2015, **48**, 3-10.

[4] G. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3-8.

[5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339-341.