Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Cobalt (II)-bridged triphenylamine and terpyridine-based donor-acceptor coordination polymer as efficient trifunctional electrocatalyst

Sugandha Singh[a], Manas K. Ghorai[b,*], Kamal K. Kar[c,*]

[a] Advanced Nanoengineering Materials Laboratory, Materials Science Programme, Indian Institute of Technology Kanpur, Kanpur 208016, India

[b] Department of Chemistry, Indian Institute of Technology, Kanpur, Kanpur 208016, India

[c] Advanced Nanoengineering Materials Laboratory, Materials Science Programme and Department of Mechanical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

[*]Corresponding Authors: Email: mkghorai@iitk.ac.in, kamalkk@iitk.ac.in

Table of contents

Materials

All commercially purchased solvents and reagents were used without further purification. Tris(4-aminophenyl)amine, cuprous iodide, tetrakis(triphenylphosphine) palladium, and bis(triphenylphosphine) palladium chloride were purchased from Sigma Aldrich Chemical Co. n-Bromobutane, iodine monochloride, hydroquinone, ethynyltrimethylsilane (TMS), tetrahydrofuran (THF), acetonitrile and triethylamine (NEt_3) were acquired from Spectrochem Pvt. Ltd., India. 1,4-dibutoxy-2,5-diiodobenzene (**2**)[1], 4-ethynylbenzaldehyde (**4**)[2] and 4'-ethynyl-2,2':6',2''- terpyridine (**7**)[3] were synthesized using literature.

Physicochemical Measurements

^{1}H NMR and ^{13}C spectra were recorded on a JEOL 500 MHz or 400 MHz spectrometer. The notations to outline splitting patterns of ^{1}H NMR signals are as follows: s = singlet, d = doublet, t = triplet, m = multiplate, dd = doublet of doublets, and ddd = doublet of doublet of doublets. Elemental analysis was conducted on PerkinElmer Series-II CNHS/O analyzer 2400. Electron Paramagnetic Resonance (EPR) spectroscopy was conducted on Bruker BioSpin GmbH in the range of 0-8000 Gauss with a microwave frequency of 9.456 GHz. UV-vis spectroscopy in solid state was recorded on a Cary 5000 UV-Vis-NIR spectrophotometer in the 400-700 nm range with a scan rate of 1.67 nm/s. Fourier transformed- infrared (FT-IR) spectroscopy was performed on Bruker-Tensor 27 using standard KBr pellets as a beam splitter in the range of 4000 to 400 cm^{-1}. The solid-state ^{13}C NMR was performed on Bruker Avance HD 500 MHz FT-NMR spectrometer in the range of 0-200 ppm. Thermogravimetric analysis (TGA) was performed using Perkin-Elmer Diamond TG/DTA analyzer (N_2 flow rate – 20 $mLmin^{-1}$, heating rate- 5°C/min, temperature range- 30° to 800°C). Powder X-ray diffraction (PXRD) pattern of **TPA-tpd-Co** was determined using Panalytical XPert X-ray diffractor with Cu K_α (λ = 1.54 Å) as X-ray source at a scan rate of 1 degree/min in the range of 3-50°. Raman spectroscopy was conducted using Horiba Jobin Yvon Lab RAM HR Raman spectrometer using He-Ne laser source (λ =632.7 nm) in ambient conditions. Brunauer–Emmett–Teller (BET) of **TPA-tpd-Co** was performed on a Quantachrome analyzer using N_2 at 77K. The sample tube was loaded with 8.38 mg of **TPA-tpd-Co** and was degassed for 5 hours at 100 °C prior to measurement. Morphological studies were carried out on JSM-7100F, JEOL Field emission scanning electron microscopy (FESEM). The sample was prepared by making uniform dispersion of **TPA-tpd-Co** in acetonitrile followed by drop-casting it on aluminum foil. Gold coating for 90 s was done

prior to FESEM analysis. Energy dispersive X-ray spectroscopy (EDAX) images were also taken on the same instrument. Transmission electron microscopy (TEM) was performed on FEI-Titan G2 300KV. Uniformly dispersed **TPA-tpd-Co** was drop-casted on a carbon-coated copper grid. X-ray photon spectroscopy (XPS) was performed on PHI 5000 Versa Prob II, FEI Inc. Inductively coupled plasma mass spectroscopy was performed on a Thermo Scientific X Series. Mott-Schottky data was determined by recording Electrochemical Impedance spectroscopy (EIS) at 1000 Hz in the potential range of 2 to -2 V vs. Ag/AgCl in 0.5 M Na_2SO_4 (pH=7) solution as electrolyte.

Electrochemical measurements

Electrode preparation

The electrocatalyst ink was prepared by adding 2mg of active material, 980µL of isopropanol and deionized water (1:1) and 20µL Nafion (5%, Alfa Aesar) and ultrasonicated for 30 min. Then, 2mg of carbon black (acetylene) was added and sonicated for additional 30 minutes. 4mm diameter of glassy carbon was used as a working electrode for rotating disk electrode (RDE) measurements. Prior to drop-cast, the glassy carbon electrode was thoroughly cleaned with alumina paste (1-3 µm) on a velvet cloth with the low forced hand in the motion of eight and further cleaned with deionized water and acetone in an ultrasonicator for 20 minutes. 10µL of the as-prepared ink was micro-pipetted on mirror-polished glassy carbon and dried under ambient conditions for oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER) tests with a catalyst loading of 0.16 mg cm^{-2}.

Measurement parameters

The as-prepared **TPA-tpd-Co** redox performance was studied on a home-build rotating disk electrode setup attached to multichannel AUTOLAB M204 Metrohm potentiostat/ Galvanostat in hydrostatic and hydrodynamic conditions. A typical 3-electrode cell was used where Ag/AgCl (sat. KCl) was used as the reference electrode, and platinum was used as the counter electrode. The obtained potentials were calibrated to Reversible Hydrogen Electrode (RHE) following Nernstian equation as, $E_{RHE} = E^0_{Ag/AgCl} + E_{Ag/AgCl} + 0.059\times pH$, where $E^0_{Ag/AgCl}$ was taken as 0.197. The obtained current was also calibrated by normalizing it to the working electrode's geometric surface area (in this work, 0.1256 cm^{-2}). The redox activity of **TPA-tpd-Co** was determined by potentiostatic cyclic voltammetry (CV), linear sweep voltammetry

(LSV), and electrochemical impedance spectroscopy (EIS). The stability of **TPA-tpd-Co** was determined by chronoamperometry. The ORR measurements were conducted with 0.1 M KOH, OER was conducted in 0.1 M, 0.2 M, and 0.5 M KOH, and HER was performed in 0.5 M H_2SO_4. Oxygen gas was purged for 30 minutes prior to the measurement for ORR, and N_2 gas was purged before OER and HER tests.

ORR measurements

The ORR activity of **TPA-tpd-Co** was recorded by CV at the sweep rate of 50 mV s^{-1} in the potential range of 0-1.2 V vs. RHE in N_2 and O_2 saturated 0.1 M KOH. LSV was recorded at 5mV s^{-1} in O_2 saturated electrolyte at varying rotation rates of 100, 400, 900, 1600, and 2500 rpm, and the viable number of electrons transferred during the reduction reaction was determined by Koutecky'-Levich (K-L) equation as given below

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{j_K} \quad (1)$$

$$B = 0.62\, nFC_{\circ}\left(D_{\circ}\right)^{\frac{2}{3}} \nu^{-\frac{1}{6}} \quad (2)$$

$$j_K = nFkC_{\circ} \quad (3)$$

where, j is the measured current density, j_L and j_K is the limiting and kinetic current density, respectively. ω is the angular rotation rate (rad/s), n is the number of electrons transferred, F is the Faraday's constant (96485 $Cmol^{-1}$), C_o is the concentration of O_2 in alkaline media (1.9 $\times 10^{-5}$ $molcm^{-3}$), D_o is the diffusion coefficient of O_2 for alkaline media (1.2 $\times 10^{-6}$ $molcm^{-3}$), ν is the kinematic viscosity of electrolyte (0.01 cm^2s^{-1}) and k is the electron transfer rate.

Tafel slope was determined by recording LSV at a slow scan rate of 1 mV s^{-1} at 1600 rpm and linearly fitted to a Tafel equation as given below

$$\eta = b \log j + a \quad (4)$$

where, η is the overpotential (mV), b is Tafel slope and j is the current density.

TPA-tpd-Co stability was determined by recording chronoamperometry at 0.61 V vs. RHE for 12 hours in O_2 saturated 0.1 M KOH at the rotation rate of 1600 rpm. The O_2 gas was

constantly bubbled throughout the test to maintain the saturation level. Electrochemical impedance spectroscopy (EIS) was recorded at varying potentials in the frequency range of 0.1 to 10^5 Hz.

OER measurements

The activity of **TPA-tpd-Co** towards OER was determined by varying the basicity of the electrolyte to 0.1, 0.2, and 0.5 M KOH. The LSV was recorded at the scan rate of 5 mV s^{-1} in the potential range of 1-2 V vs. RHE at 0 and 1600 rpm. The Tafel slope was determined by recording the LSV at a slow scan rate of 1 mV s^{-1} at 1600 rpm. The cyclic stability of **TPA-tpd-Co** was determined by recording LSV at a scan rate of 50 mV s^{-1} for 100 cycles in 0.5M KOH and 300 cycles in 0.2 M KOH in the potential range of 1-2 V vs. RHE at 1600 rpm. Electrochemical impedance spectroscopy (EIS) was recorded at varying potentials in the frequency range of 0.1 to 10^5 Hz. Commercial 40 wt% Pt/C and RuO_2 were also measured for comparison.

Further electrochemical calculations of **TPA-tpd-Co** in OER were followed by the determination of electrochemical active surface area (EASA). The double layer capacitance (C_{dl}) and specific capacitance (C_s) were determined by recording CV in the non-Faradaic region at varying scan rates with **TPA-tpd-Co** loaded GC and bare GC. The EASA is given as

$$EASA = \frac{C_{dl}}{C_s} \quad (5)$$

The roughness factor is the ratio of EASA to the geometrical surface area, given as

$$RF = \frac{EASA}{GSA} \quad (6)$$

The CV was recorded in the redox-active potential range at varying scan rates to determine the active number of cobalt atoms. Anodic peak current was utilized to determine the surface coverage (τ_0), which unveils the active cobalt atoms.

$$slope = \frac{n^2F^2\tau_{\circ}A}{4RT} \quad (7)$$

where, n is the no. of electrons taking part in the redox reaction, F is the Faraday's constant (96485 C mol^{-1}), A is the Geometric surface of glassy carbon (cm^{-2}), τ_o is the surface coverage, R is the universal gas constant (VC/K/mol), T is the Temperature (K)

Turn over frequency was determined by using the below-mentioned equation

$$TOF = \frac{(Avogadro's\ no) \times\ j\ (1\ mA/cm^2)}{4 \times RF \times F \times no\ of\ active\ sites} \quad (8)$$

HER measurements

The HER activity of **TPA-tpd-Co** was studied by recording LSV in 0.5 M H_2SO_4 at a scan rate of 5 mV s^{-1} in N_2 saturated electrolyte at 1600 rpm cycles in the potential range of 0 to -1 V vs. RHE. Tafel slope was determined by recording LSV at a slow scan rate of 1 mV s^{-1} at 1600 rpm. To explore the stability of the catalyst, LSV was run at a sweep rate of 50 mV s^{-1} at 1600 rpm for 500 cycles in the potential range of 0 to -1 V vs. RHE. For chronoamperometry, the overpotential required to acquire a current density of 10 mA cm^{-2} (-0.48 V vs. RHE) was utilized to investigate the stability for 12 hours. Electrochemical impedance spectroscopy (EIS) was recorded at varying potentials in the frequency range of 0.1 to 10^5 Hz.

The EASA and RF for HER were determined by following the same procedure as OER by recording CV in the non-Faradaic region at varying rotation rates in 0.5 M H_2SO_4 and calculated by following equations (5) and (6). The number of active sites was determined by recording CV at the current onset region at varying scan rates and taking current values at an overpotential of 250 mV. The TOF was determined at an overpotential of 10 $mAcm^{-2}$ (428 mV) by utilizing the given formula below

$$TOF = \frac{j \times SA}{n \times F \times N} \quad (9)$$

Where j is the current density, SA is the surface area, n is the number of electrons (here, 2), F is Faraday's constant and N is the number of active sites.

Zn-air battery fabrication

To determine the application of our as-prepared electrocatalyst, a conventional aqueous Zn-air battery was fabricated. Firstly, for the cathode, a chemical ink was prepared using 0.5 mg

TPA-tpd-Co, 0.5 mg carbon black (acetylene), and 10 µL Nafion in 500 µL isopropanol. The solution was ultrasonicated for 90 minutes for thorough dispersion and deposited on the gas diffusion layer (GDL) (Toray Carbon 60, Alfa Aesar, 200 µm). Then, the acquired GDL was dried at 60°C for 4 hours. Zn foil (Sigma Aldrich, 250 µm) was used as an anode. 6M KOH and 0.2 M Zinc acetate were used as an aqueous electrolyte, and Whatman 40 filter paper soaked in the electrolyte was used as a separator. The GDL geometric diameter was kept at 1 cm. The performance was studied using galvanostatic charge-discharge and chronopotentiometry. For comparison, GDL was prepared using 0.5 mg (1:1) Pt/C (40%) and RuO_2 by following a similar procedure as our polymer.

Synthesis

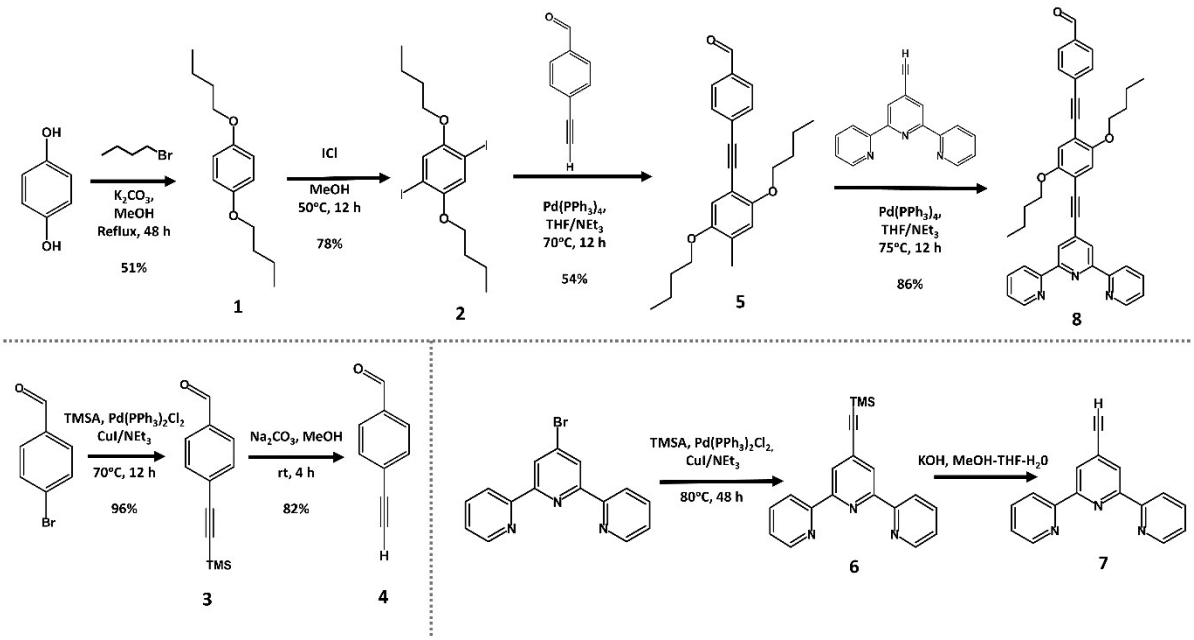
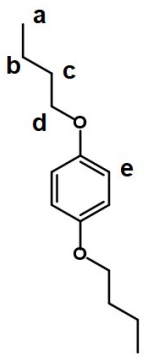


Fig S1. Complete synthesis scheme for **8**



Synthesis of 1,4-dibutoxybenzene (1): A single neck round bottom flask was loaded with hydroquinone (10 gram, 110.11 mmol), n-bromobutane (31.1 gram, 137.02 mmol), and methanol (250 mL). The reaction mixture was allowed to stir over a magnetic stirrer, then K_2CO_3 (31.3 grams, 227 mmol) was added to the reaction mixture and refluxed for 48 hours. After the completion of the reaction, the reaction mixture was cooled to room temperature and was evaporated to dryness in a rotary evaporator. The solid residue was purified by column chromatography (SiO_2, Ethyl acetate/Hexane = 1:25, R_f = 0.69)

to afford white colored solid as our compound **1**. m.p. = 40-42°C, yield: 51% (10.31 gm, 82.6 mmol). IR (KBr, $1/\upsilon_{max}$): 3048, 2956, 2934, 2872, 1867, 1738, 1588, 1509, 1470, 1396, 1287, 1265, 1233, 1145, 1123, 1071, 1043, 1013, 974, 906, 872, 829, 767, 740, 705, 534, 523 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.96 (t, ^{3}J = 7.2 Hz, 6H, a), 1.45-1.51 (m, 4H, b), 1.70-1.76 (m, 4H, c), 3.90 (t, ^{3}J = 6.5 Hz, 4H, d), 6.81 (s, 4H, e) ppm; ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ = 13.9, 19.3, 31.5, 68.4, 115.5, 153.3 ppm; Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.61; H, 10.12.

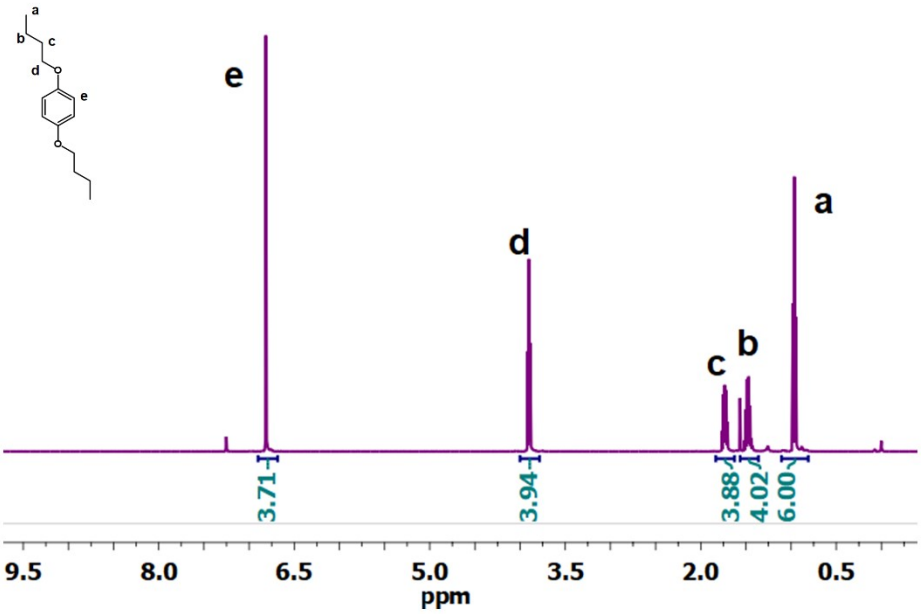


Fig S2. (a) ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **1**

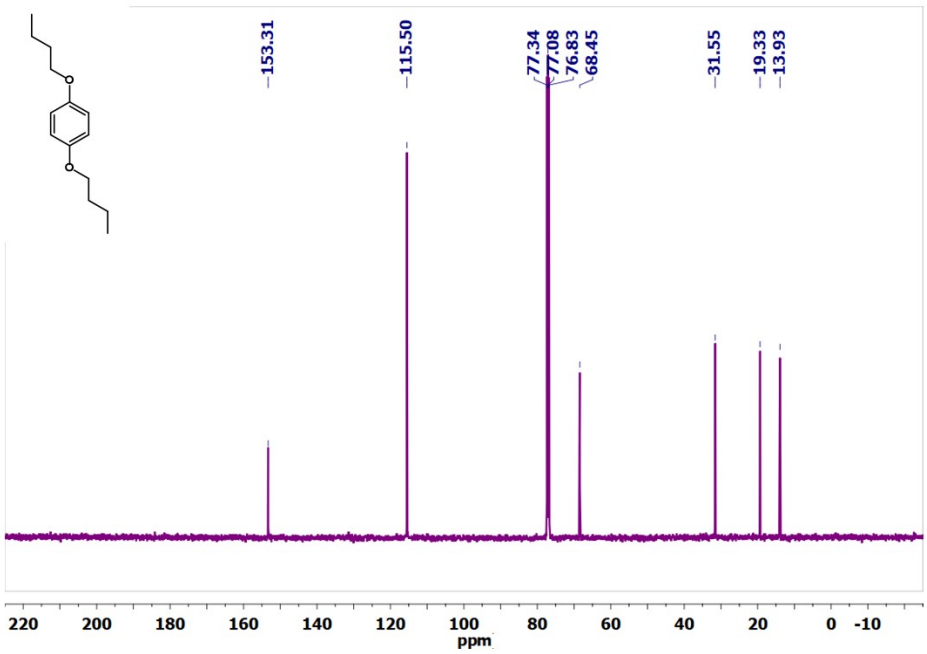


Fig S2 (b) ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of compound **1**

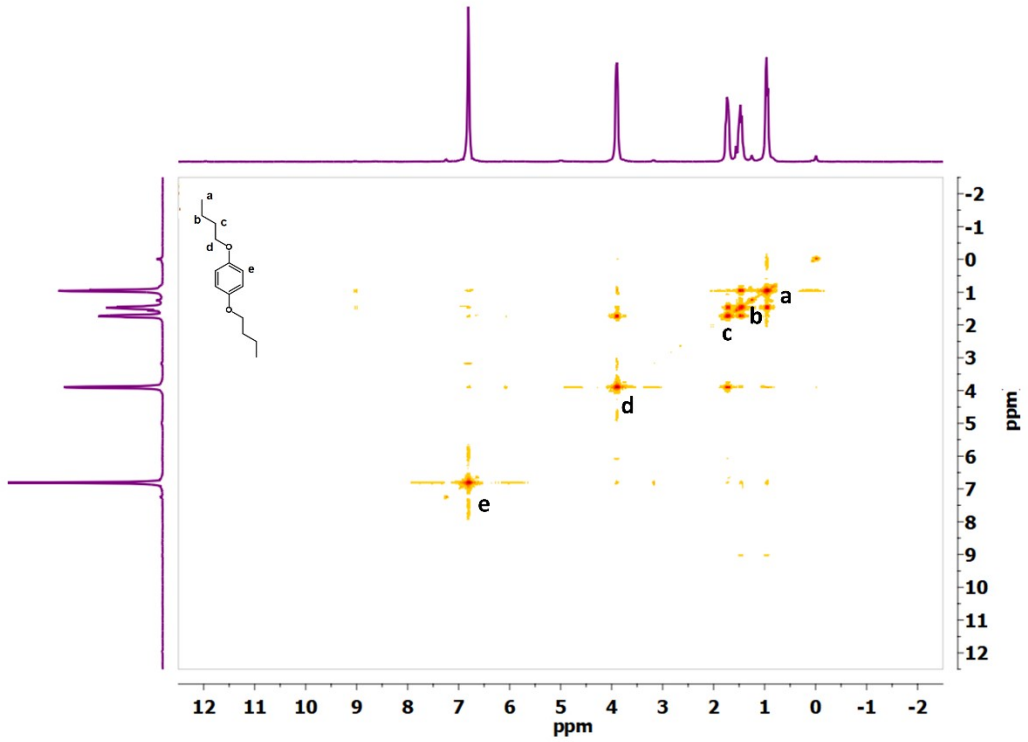
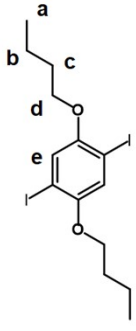


Fig S2 (c) ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 500 MHz) of compound **1**

Synthesis of 1,4-dibutoxy-2,5-diiodobenzene (2): A single neck round bottom flask was loaded with compound **1** (10.31 grams, 46.4 mmol) in methanol (20



mL) and kept at ice-cold condition. A separate round bottom flask was charged with methanol (25 mL) in an ice-cold condition, and iodine chloride (17 mL) was added drop wise to it. Then the solution was added to the prior mentioned flask containing 1,4-dibutoxybenzene, and the reaction solution was refluxed overnight. All the glass wares were immediately quenched with aqueous KOH. After completion of the reaction, the reaction vessel was cooled to room temperature, and the reaction solution was filtered over Whatman 40 filter paper and washed with methanol to obtain pink colored solid. The residue was further purified to remove ICl by column chromatography (SiO_2, Hexane, R_f = 0.57) to afford white colored solid as our compound **2**. m.p.= 78-80°C, yield: 78% (17.2 g, 36.2 mmol). IR (KBr, $1/\upsilon_{max}$): 2956, 2940, 2925, 2868, 1487, 1467, 1460, 1451, 1396, 1377, 1351, 1271, 1260, 1208, 1161, 1122, 1054, 1032, 1003, 904, 850, 791, 741, 620, 512,434 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 0.97 (t, ^3J = 7.5 Hz, 6H, a), 1.49-1.56 (m, 4H, b), 1.75-1.80 (m, 4H, c), 3.92 (t, ^3J = 6.5, 4H, d), 7.16 (s, 2H, e) ppm; ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ = 13.9, 19.4, 31.3, 70.1, 86.4, 122.9, 152.9 ppm; Anal. Calcd for $C_{14}H_{20}I_2O_2$: C, 35.47; H, 4.25. Found: C, 35.32; H, 4.11.

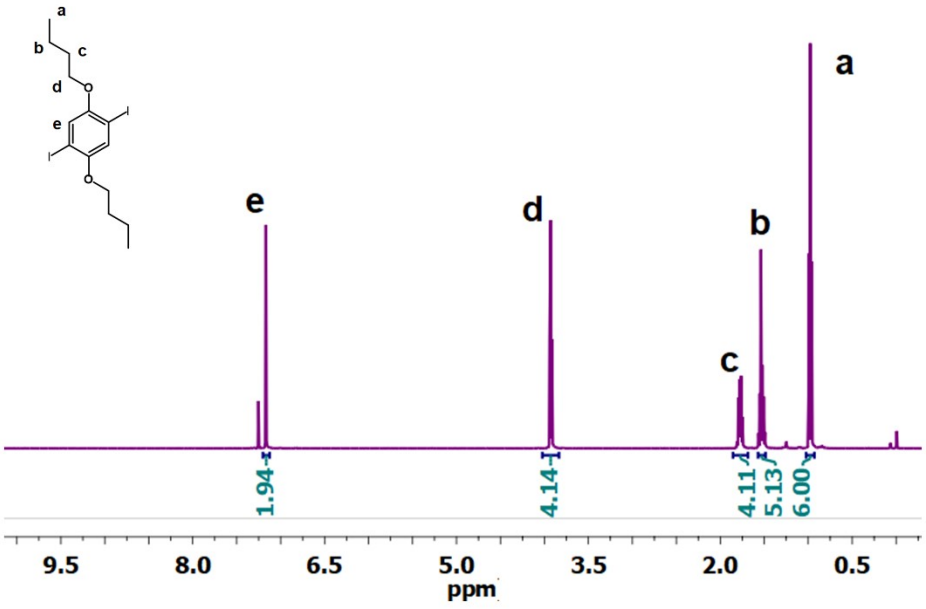


Fig S3. (a) ^1H NMR spectrum ($CDCl_3$, 500 MHz) of compound **2**

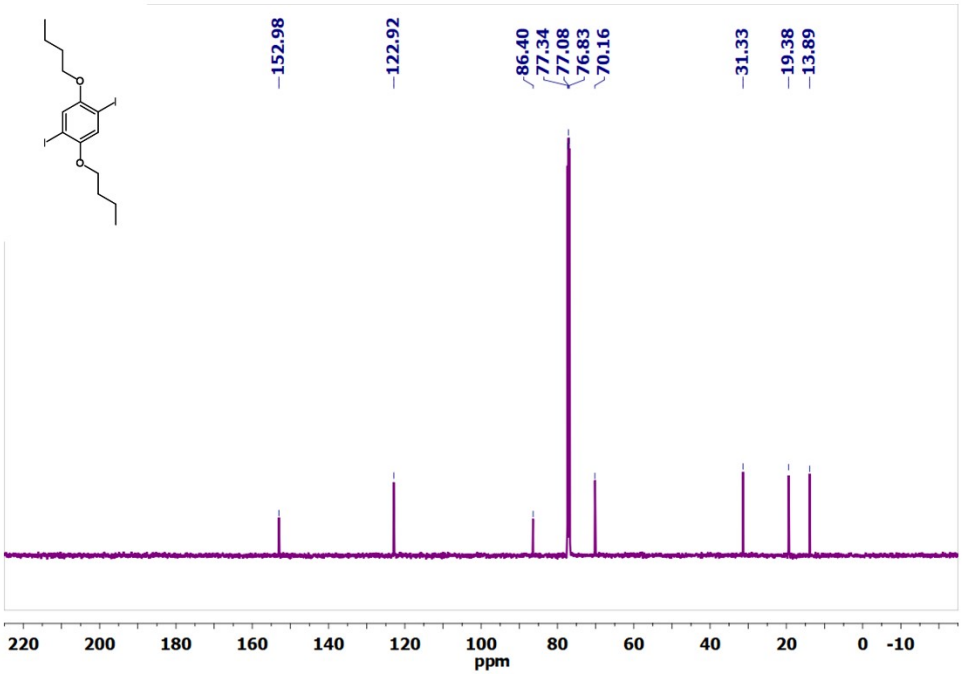


Fig S3 (b) ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of compound **2**

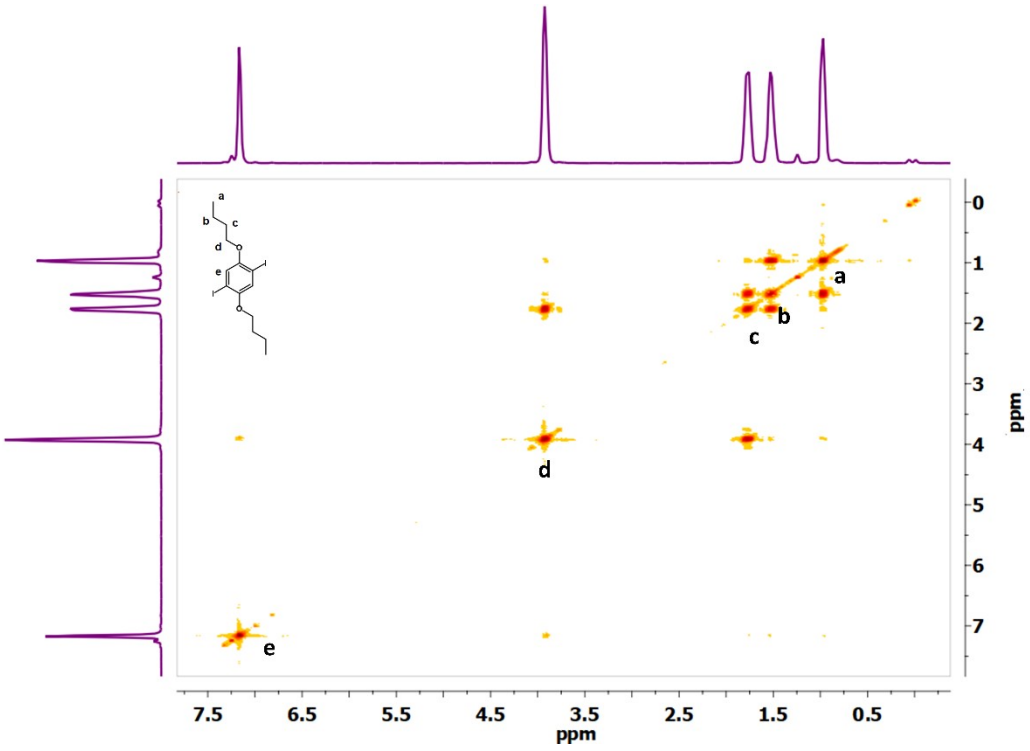


Fig S3 (c) ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 500 MHz) of compound **2**

Synthesis of (triethylsilyl)ethynyl benzaldehyde (3): A single neck round bottom flask was loaded with 4-bromobenzaldehyde (1 gm, 5.40 mmol), bis(triphenylphosphine) palladium chloride (378 mg, 0.54 mmol), copper iodide (206 mg, 1.08 mmol), triethylamine (10 mL), tetrahydrofuran (20 mL). To the reaction mixture, ethynyltrimethylsilane (3.1 mL, 21.6 mmol) was added at last and the reaction vessel was sealed immediately. The reaction mixture was heated to 70°C for 12 hours in an oil bath for completion of the silylation process. After completion of the reaction, the reaction mixture was cooled to room temperature and was evaporated to dryness in a rotary evaporator. The solid residue was purified by column chromatography (flash SiO_2, ethyl acetate/ hexane = 1:49, R_f = 0.62) to obtain brown colored solid as our compound **3**. m.p. =100-102 °C, yield: 96% (1.05 gm, 5.18 mmol). IR (KBr, $1/\upsilon_{max}$): 2959, 2925, 2852, 2730, 2671, 2547, 2157, 1683, 1602, 1561, 1502, 1424, 1313, 1293, 1282, 1251, 1218, 1205, 1166, 1126, 1103, 1015, 956, 862, 842, 787, 774, 759, 697, 660, 636, 556, 534 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 0.25 (s, 9H, a), 7.60 (d, ^3J = 8.5 Hz, 2H, b), 7.80 (d, ^3J = 8.5 Hz, 2H, c), 10.0 (s, 1H, d) ppm; ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ = 0.1, 99.1, 103.9, 129.4, 132.5, 135.6, 191.4 ppm; Anal. Calcd for $C_{14}H_{22}O_2$: C, 71.24; H, 6.97. Found: C, 61.43; H, 7.04.

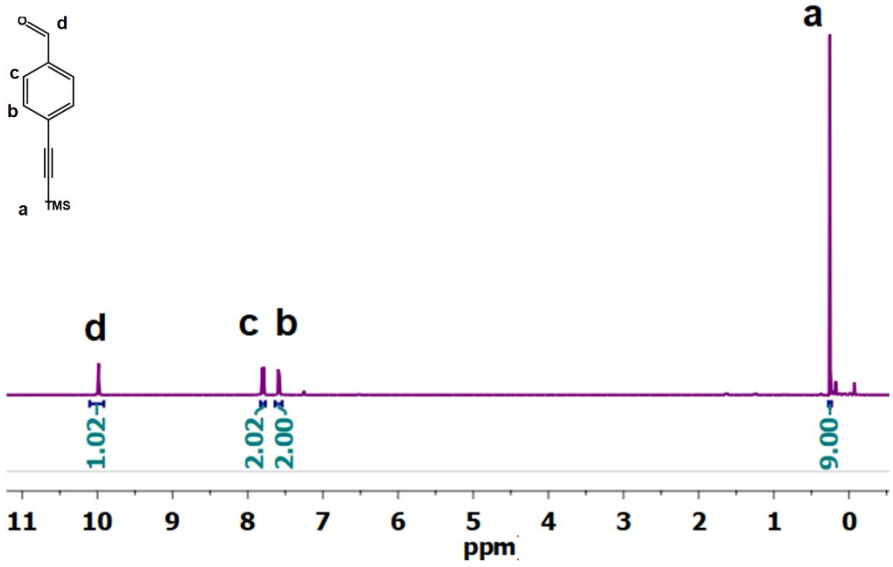


Fig S4. (a) ^1H NMR spectrum ($CDCl_3$, 500 MHz) of compound **3**

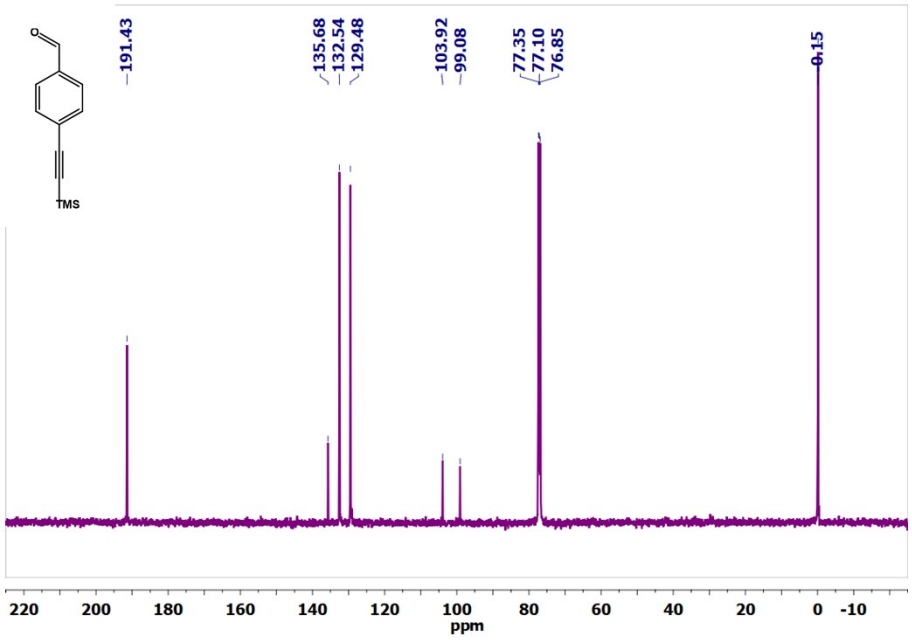


Fig S4 (b) ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of compound **3**

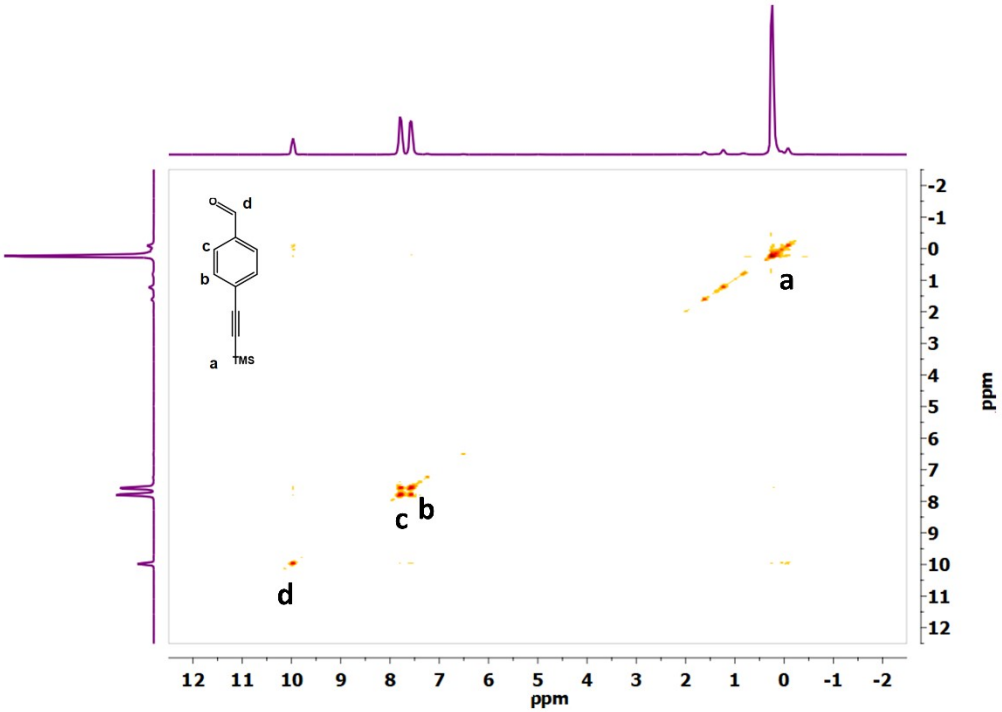


Fig S4 (c) ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 500 MHz) of compound **3**

Synthesis of 4-ethynylbenzaldehyde (4): Compound **3** (1.0 gram, 4.94 mmol) was desilylated by charging it to a solution of sodium carbonate (0.52 gm, 4.94 mmol) in methanol (30mL) (1:1) for 4 hours in ambient condition. After completion of desilyation process, the solution was filtered over Whatman 40 filter paper to remove Na_2CO_3, and the filtrate was evaporated to dryness in a rotary evaporator. The solid residue was purified by column chromatography (flash SiO_2, ethyl acetate/ hexane = 3:97, R_f = 0.51) to afford dark yellow colored solid as our compound **4**. m.p. = 95-97°C, yield: 82% (527 mg, 4.05 mmol). IR (KBr, $1/\upsilon_{max}$): 3220, 2923, 2850, 2741, 2100, 1701, 1685, 1605, 1562, 1389, 1304, 1288, 1207, 1164, 1013, 847, 829, 739, 681, 580, 530, 408 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 3.28 (s, 1H, a), 7.63 (d, ^3J = 8.5 Hz, 2H, b), 7.83 (d, ^3J = 8.5 Hz, 2H, c), 10.0 (s, 1H, d) ppm; ^{13}C {^1H} NMR: (125 MHz, $CDCl_3$) δ = 81.1, 82.7, 128.4, 129.5, 132.7, 136.0, 191.4 ppm; Anal. Calcd for C_9H_6O: C, 83.06; H, 4.65. Found: C, 83.28; H, 4.71.

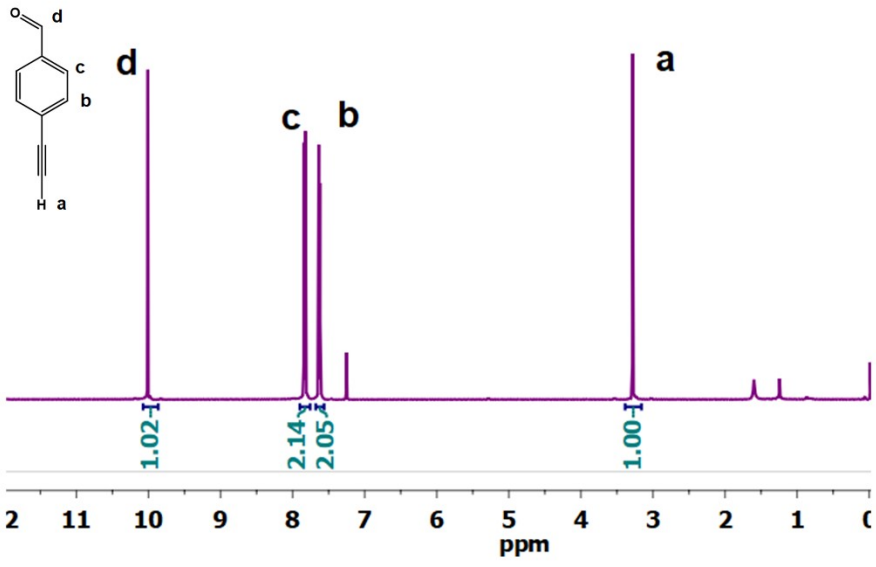


Fig S5. (a) ^1H NMR spectrum ($CDCl_3$, 500 MHz) of compound **4**

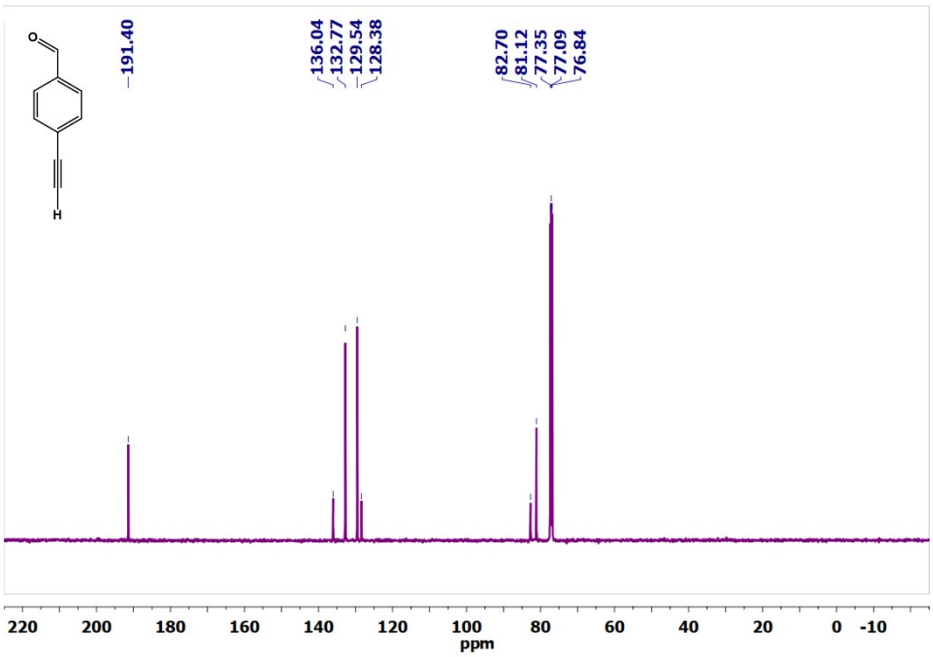


Fig S5 (b) ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of compound **4**

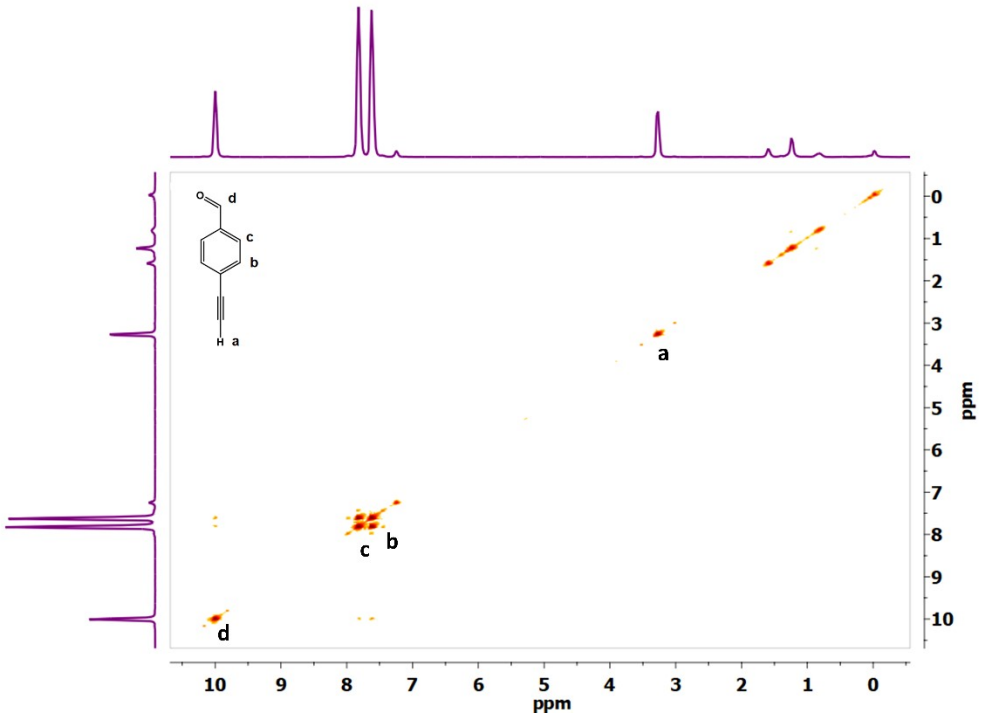
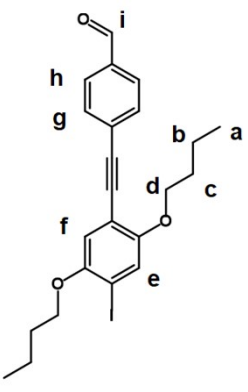


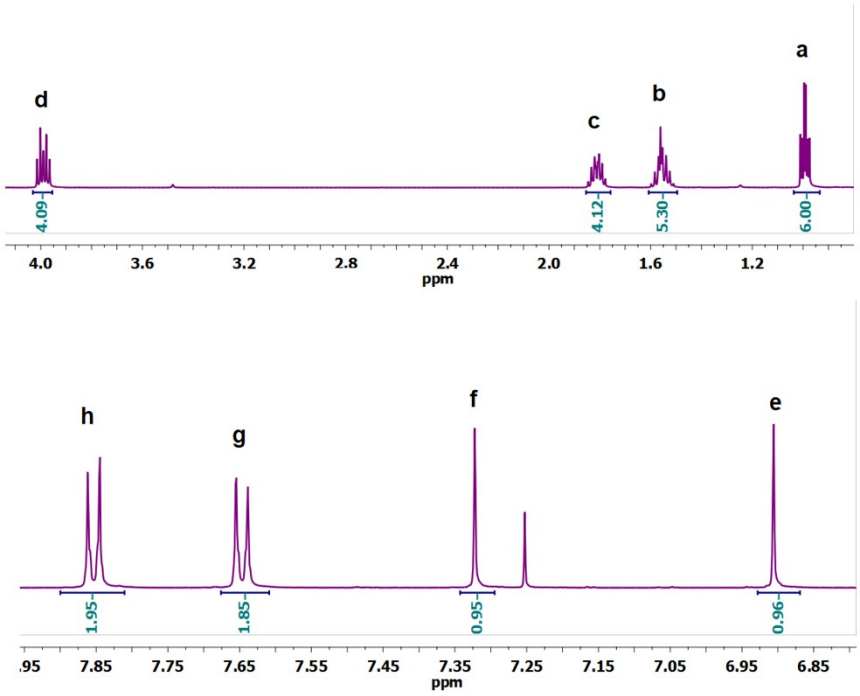
Fig S5 (c) ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 500 MHz) of compound **4**

Synthesis of 4-((2, 5-dibutoxy-4iodophenyl) ethynyl) benzaldehyde (5):

A Schlenk flask was charged with 1,4-dibutoxy-2,5-diiodobenzene (546



mg, 1.152 mmol), 4-ethynylbenzaldehyde (100 mg, 0.768 mmol), tetrahydrofuran (10 mL) and triethylamine (5 mL). The resulting reaction mixture was degassed with Argon by a freeze-pump-thaw method which was followed by the addition of tetrakis(triphenylphosphine) palladium (88.7 mg, 0.0768 mmol) to the reaction vessel. Again, the reaction vessel was degassed by the above-mentioned method. The obtained reaction mixture was heated to 70°C for 12 hours in an oil bath. After completion of the reaction, the reaction mixture was cooled to room temperature and evaporated to dryness in a rotary evaporator. The solid residue was purified by column chromatography (SiO_2, ethyl acetate/ hexane = 1:39, R_f = 0.52) to afford a light yellow-colored solid as compound **5**. mp = 78-80°C, yield: 54% (296 mg, 0.62 mmol). IR (KBr, 1/υ_{max}): 2957, 2928, 2871, 2730, 2209, 1702, 1600, 1560, 1506, 1485, 1464, 1380, 1301, 1269, 1165, 1100, 1066, 1025, 973, 844, 827, 771, 528 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 0.97-1.01 (m, 6H, a), 1.61-1.45 (m, 4H, b), 1.90-1.73 (m, 4H, c), 3.89 - 4.12 (m, 4H, d), 6.91 (s, 1H, e), 7.32 (s, 1H, f), 7.65 (d, ^3J = 8.2 Hz, 2H, g), 7.85 (d, ^3J =8.2 Hz, 2H, h), 10.01 (s, 1H, i) ppm; ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ = 13.9 (2C), 19.3, 19.4, 31.3, 31.3, 69.6, 69.9, 88.8, 89.9, 93.3, 112.8, 116, 123.9, 129.6, 129.8, 132, 135.4, 152, 154.6, 191.4 ppm. Anal. Calcd for $C_{23}H_{25}IO_3$: C, 57.99; H, 5.29. Found: C, 56.82; H, 5.40.



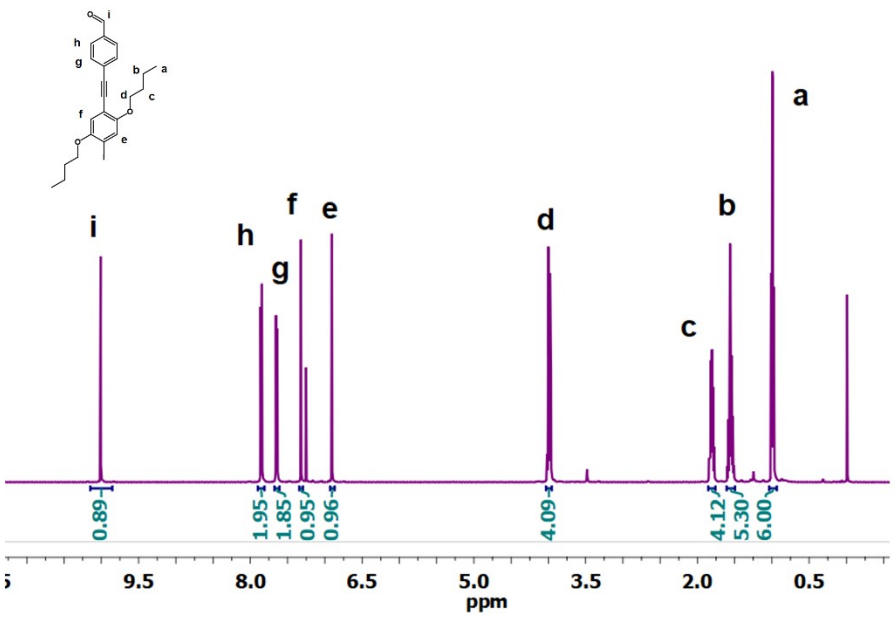


Fig S6. (a) ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **5**

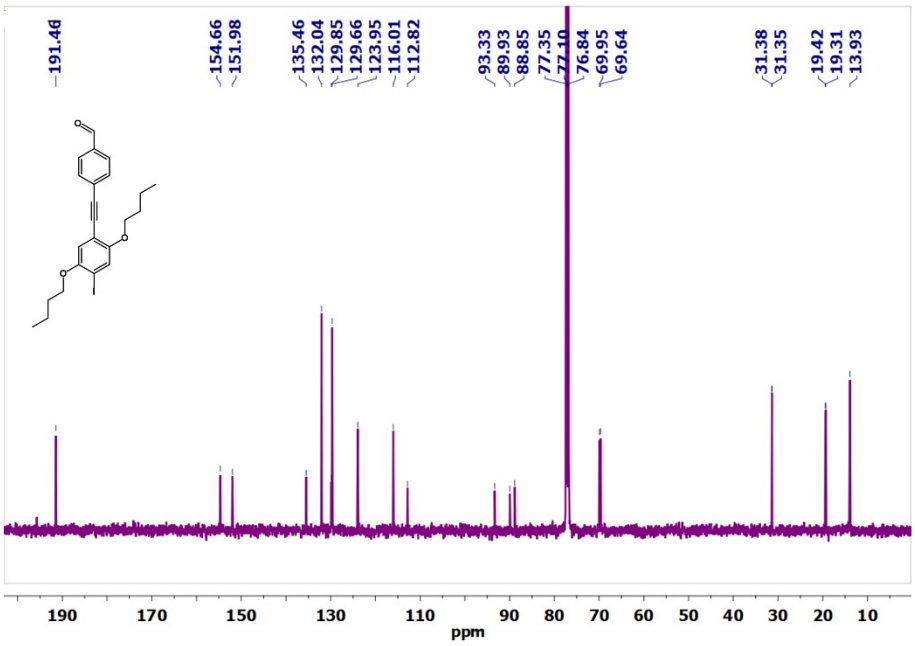


Fig S6 (b) ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of compound **5**

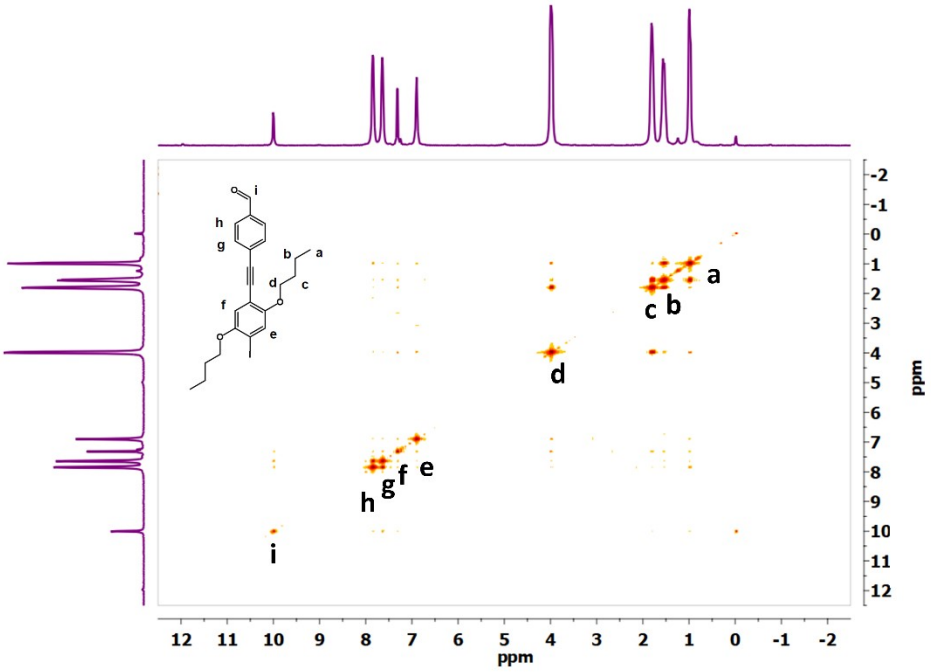
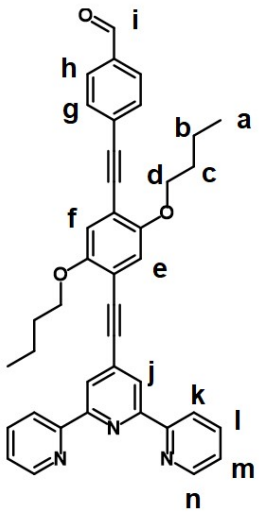
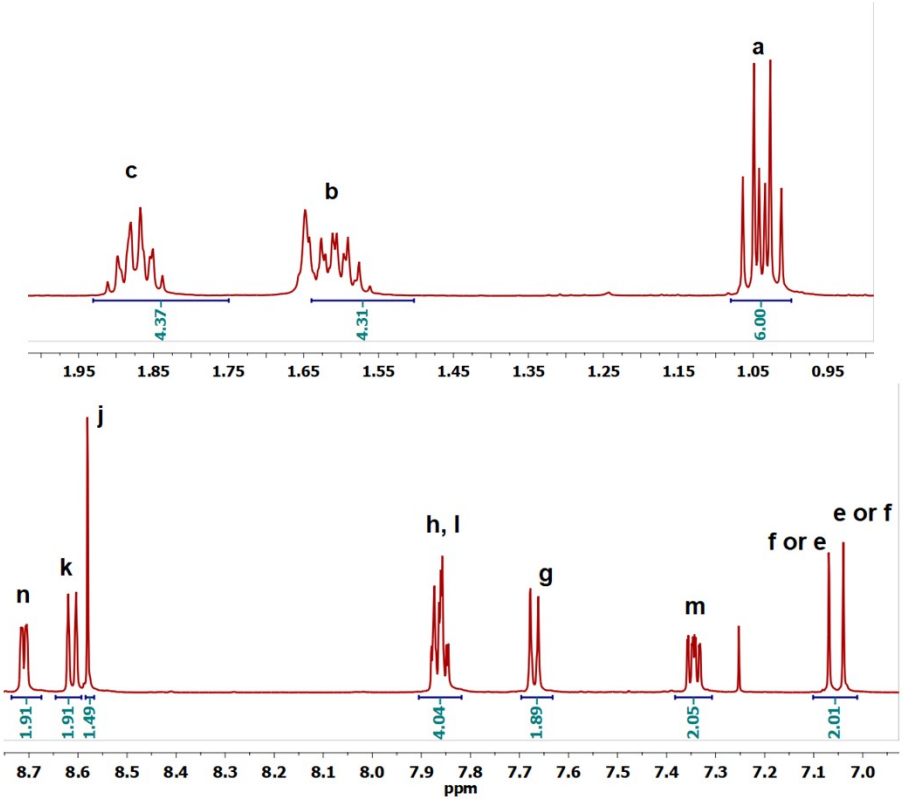


Fig S6 (c) ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 500 MHz) of compound **5**

Synthesis of 4-((4-([2, 2': 6', 2'' – terpyridine]-4'-ylethynyl)-2, 5-dibutoxyphenyl)ethynyl)benzaldehyde (8): A Schlenk flask was loaded with compound **5** (100 mg 0.209 mmol), compound **7** (54 mg, 0.209 mmol), tetrahydrofuran (5 mL) and triethylamine (5 mL). The resulting reaction mixture was degassed with Argon by the freeze-pump-thaw method, followed by the addition of tetrakis(triphenylphosphine) palladium (24.2 mg, 0.0209 mmol) to the reaction solution. Again, the reaction vessel was degassed with priori mentioned method. The obtained reaction mixture was heated to 70°C for 12 hours under an argon environment in an oil bath. After completion of the reaction, the reaction mixture was cooled to room temperature, sonicated and filtered over Whatman 40 filter paper, and washed with methanol to obtain yellow-colored residue as our pure product. To fetch the compound from filtrate, the filtrate was evaporated to dryness in a rotary evaporator, and the solid residue was purified by column chromatography (neutral alumina, dichloromethane/ hexane = 1:1, R_f = 0.35) to afford yellow-



colored solid as our pure product. m.p. = 140-142°C, yield: 86% (109 mg, 180 µmol). IR (KBr, $1/\upsilon_{max}$): 3055, 2957, 2928, 2870, 2731, 2210, 1699, 1599, 1583, 1566, 1510, 1495, 1466, 1445, 1419, 1390, 1301, 1278, 1207, 1165, 1119, 1095, 1068, 1026, 924, 889, 848, 828, 792, 775, 743, 690, 660, 619, 563, 520, 404 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.01-1.06 (m, 6H, a), 1.57- 1.64 (m, 4H, b), 1.84-1.91 (m, 4H, c), 4.06-4.09 (m, 4H, d), 7.04 (s, 1H, e or f), 7.07 (s, 1H, f or e), 7.35 (ddd, 2H, ^{3}J = 7.4 Hz, ^{3}J = 4.5 Hz, ^{4}J = 0.9 Hz, m), 7.68(d, ^{3}J = 8.5 Hz, 2H, g), 7.85-7.88 (m, 4H, 10-H, h, l), 8.58 (s, 2H, j), 8.62 (d, ^{3}J = 8.0 Hz, 2H, k), 8.72 (dd, ^{3}J = 4.5 Hz, ^{4}J = 1.0 Hz, 2H, n), 10.02 (s, 1H, i) ppm. ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ = 14.0, 19.3, 19.4, 31.4, 31.4, 69.4, 69.6, 90.2, 93.2, 94.2, 117.2, 117.3, 121.3, 122.8, 124.0, 129.6, 132.1, 136.9, 149.2, 153.9, 155.6, 155.8, 191.4 ppm. Anal. Calcd for $C_{40}H_{35}N_3O_3$: C, 79.31; H, 5.82; N, 6.94. Found: C, 79.58; H, 5.66; N, 7.28.



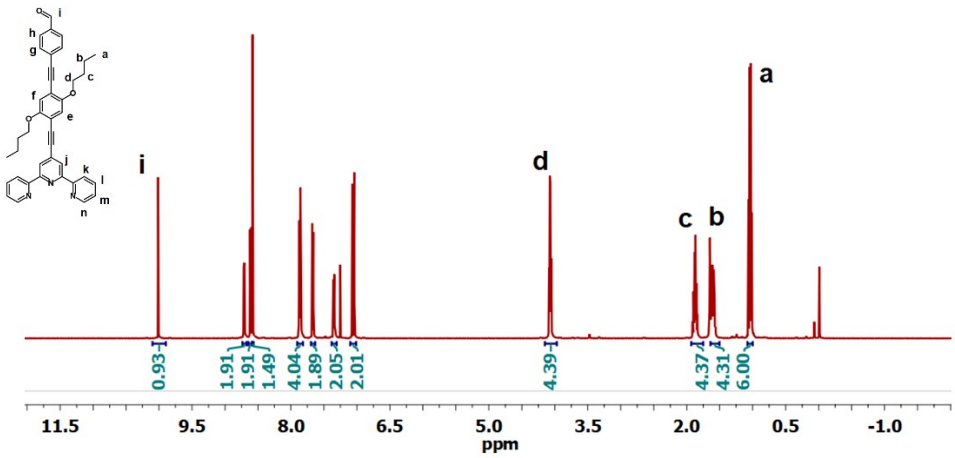


Fig S7. (a) ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **8**

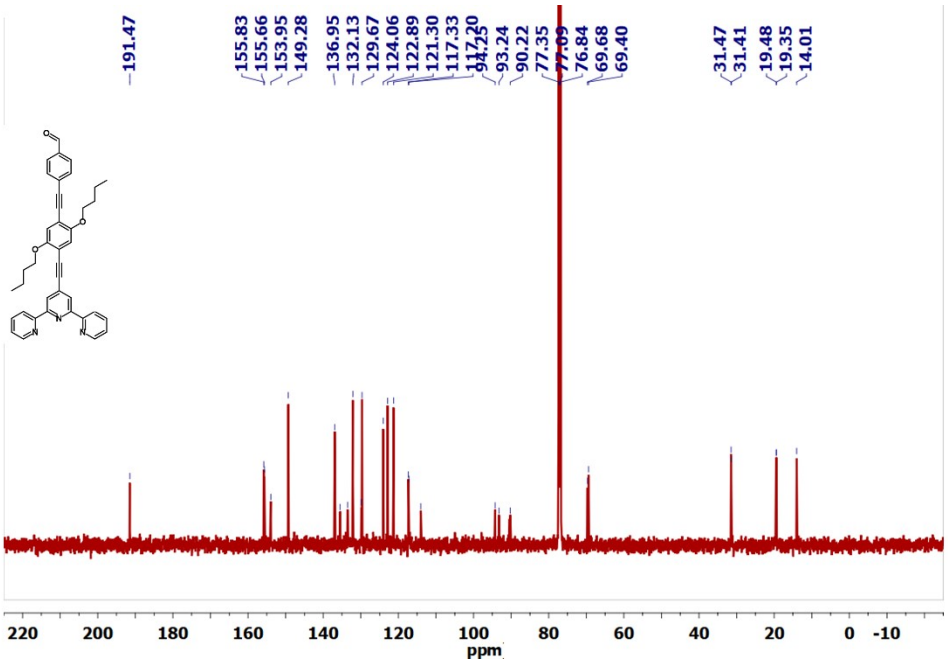


Fig S7 (b) ^{13}C NMR spectrum ($CDCl_3$, 125 MHz) of compound **8**

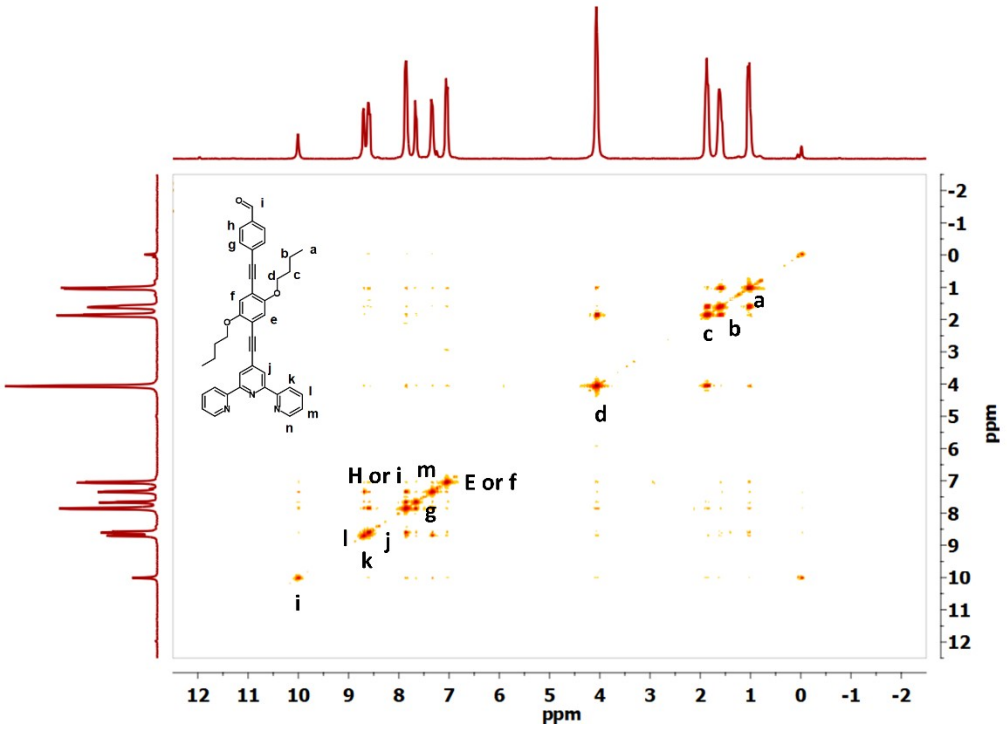


Fig S7 (c) ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 500 MHz) of compound **8**

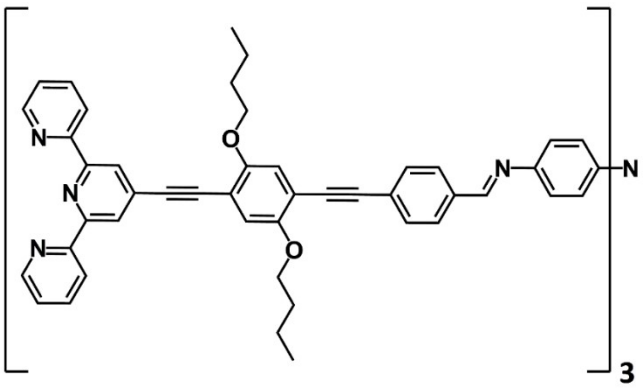


Fig S8. Chemical structure of **TPA-tpd** ligand

Synthesis of TPA-tpd-Co

A single neck round bottom flask was charged with compound **8** (9.4 mg, 0.0155 mmol) and N^1, N^1- bis(4-aminophenyl) benzene-1,4-diamine (1.48 mg, 0.0051 mmol) and acetonitrile (2mL) were added to it. The reaction mixture was refluxed for 6 hours in an oil bath. After 6 hours to the dark red solution, hydrated cobalt chloride (1.82 mg, 0.0076 mmol) was added and allowed to stir for another 18 hours. The resulting solution was evaporated, and the solid

residue was extracted as our polymer. It was further dried under vacuum at 80°C for 2 hours to afford black-colored compound as our pure product. Yield: 10.2 mg, IR (KBr, $1/\upsilon_{max}$): 3412, 3048, 2953, 2866, 2206, 1691, 1596, 1491, 1469, 1414, 1318, 1273, 1201, 1009, 832, 786, 722 cm^{-1}. Anal. Calcd for $C_{140}H_{123}Co_3N_{13}O_6$: C, 74.39; H, 5.49; N, 8.06. Found: C, 65.90; H, 5.12; N, 7.02.

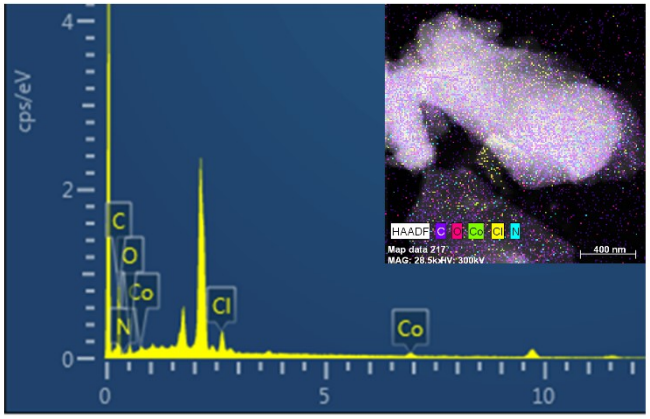


Fig S9. EDAX spectrum of **TPA-tpd-Co**

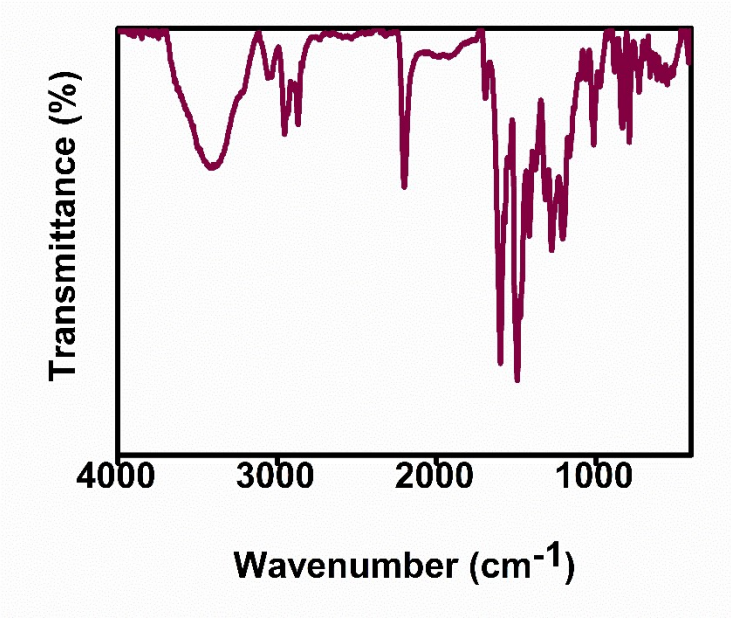


Fig S10. Fourier-transform infrared (FTIR) spectrum of **TPA-tpd-Co**

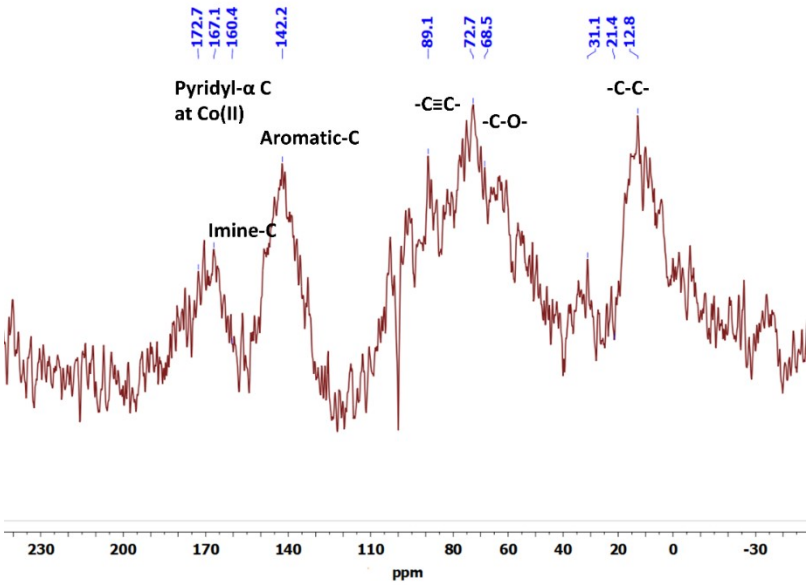


Fig S11. Solid state ^{13}C NMR spectrum of **TPA-tpd-Co**

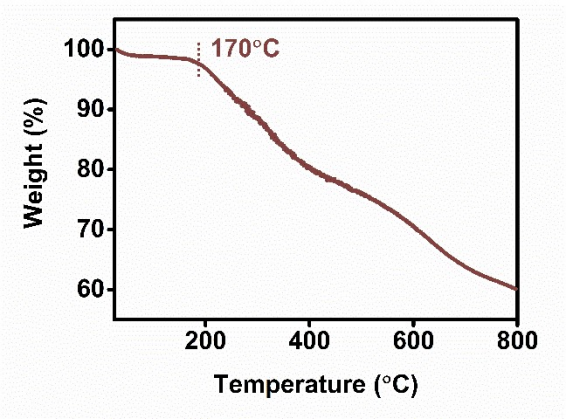


Fig S12. Thermogravimetric analysis (TGA) plot of **TPA-tpd-Co**

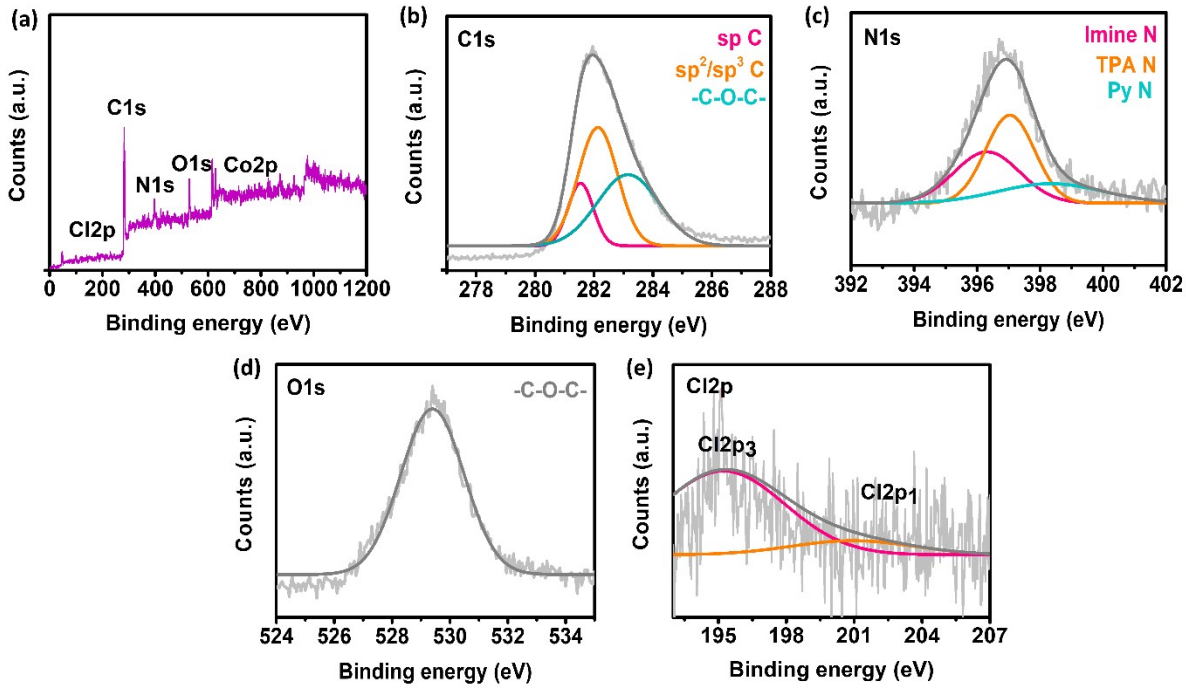


Fig S13. X-ray photon spectroscopy (XPS) of **TPA-tpd-Co,** (a) Full spectrum, (b) deconvoluted C1s, (c) deconvoluted N1s, (d) deconvoluted O1s and, (e) deconvoluted Cl2p spectrum

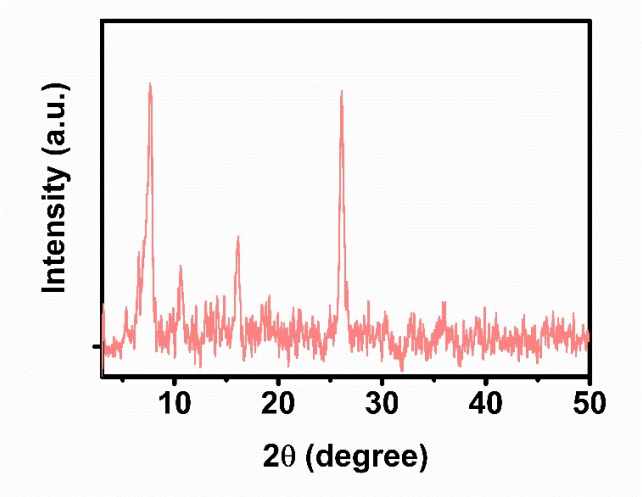


Fig S14. Powder X-ray diffraction (XRD) pattern of **TPA-tpd-Co**

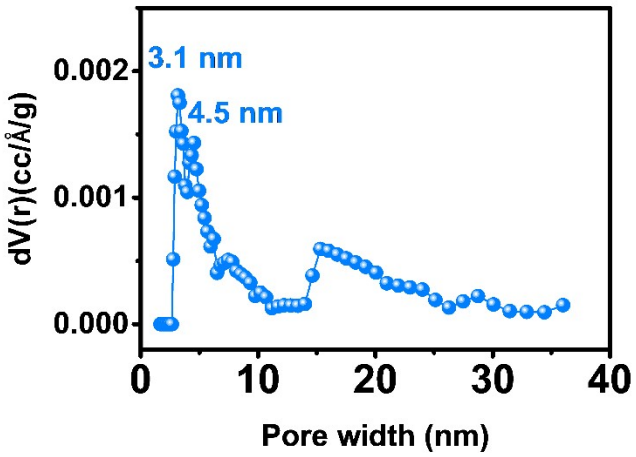


Fig S15. Pore size distribution calculated from NLDFT method using N_2 adsorption data of **TPA-tpd-Co**.

Determination of conduction band and valence band from Mott-Schottky analysis

The valence band edge ($E_{VB\ edge}$) potential for **TPA-tpd-Co** was determined with the help of the Mott-Schottky plot and optical bandgap obtained from the Tauc plot. The conduction band edge ($E_{CB\ edge}$) was assigned considering the flat band potential, which came out to be -0.99 V. The position of the valence band edge was calculated as follows:

$$E_{VB\ edge} = E_{CB\ edge} + \text{optical bandgap} \quad (10)$$

$E_{CB\ edge} = E_{fb} = -0.99$ V

$E_{VB\ edge} = -0.99 + 2.0 = 1.01$ V

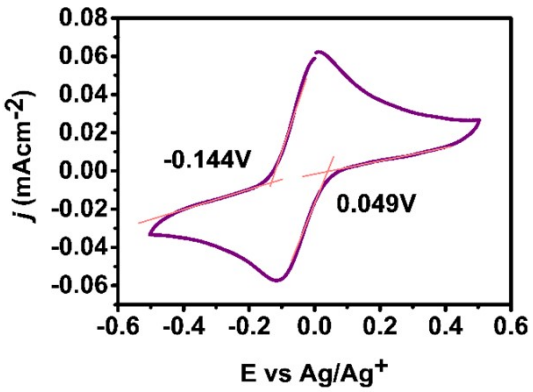


Fig S16. Cyclic voltammetry (CV) of TPA-tpd-Co recorded in 0.1 M tetrabutylammonium perchlorate (TBAP) solution in anhydrous acetonitrile with respect to $Ag/AgNO_3$

To determine the electrochemical bandgap of TPA-tpd-Co, the cyclic voltammetry (CV) was recorded under non-aqueous conditions. The Ag/Ag^+ non-aqueous reference electrode filled with 0.01 M $AgNO_3$ and 0.1 M TBAP solution in anhydrous acetonitrile was used. The obtained redox potentials were converted into RHE before proceeding with bandgap calculations. The equation used for conversion is as follows

$$E_{RHE} = E^0_{Ag/Ag+} + E_{Ag/Ag+} + 0.059\times pH \quad (11)$$

where, E_{RHE} = corresponding potential in RHE,

$E_{Ag/Ag+}$ = standard electrode potential for Ag/Ag^+ couple,

E = observed potential using Ag/Ag^+ couple

Utilizing equation (11), the oxidation and reduction potentials came out to be 1.224 V and 1.096 V, respectively.

E_{oxRHE} = 0.799 + 0.012 + 0.413 = 1.224 V

E_{redRHE} = 0.799 + (-0.116) + 0.413 = 1.096 V

The onset oxidation and reduction potentials were found to be 1.068 V and 1.260 V, respectively.

E^{onset}_{oxRHE} = 0.799 + (-0.144) + 0.413 = 1.068 V

E^{onset}_{redRHE} = 0.799 + (0.049) + 0.413 = 1.261 V

The following equation (12) and (13) were utilized to determine the experimental electrochemical HOMO and LUMO levels in terms of eV

$$E\ (HOMO) = -e\ [E^{onset}_{oxRHE} + 4.44] \quad (12)$$

$$E\ (LUMO) = -e\ [E^{onset}_{redRHE} + 4.44] \quad (13)$$

The calculated HOMO and LUMO levels came out to be -5.09 eV and -2.76 eV, respectively, giving the bandgap of **2.33 eV**.

E (HOMO) = -e [1.068 - 0.42 + 4.44] = **-5.09 eV**

E (LUMO) = -e [-1.261 - 0.42 + 4.44] = **-2.76 eV**

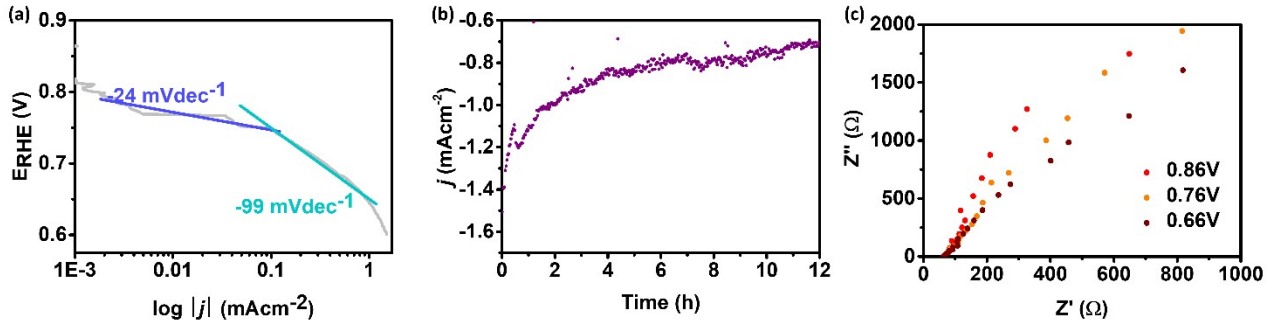


Fig S17. (a) Tafel plot recorded at 1 mVs^{-1} at 1600 rpm O_2 saturated 0.1 M KOH, (b) chronoamperometry at 0.61 V at 1600 rpm in O_2 saturated 0.1 M KOH, and (c) Nyquist plot In the frequency ranging from 0.1 to 10^5Hz in 0.1 M KOH

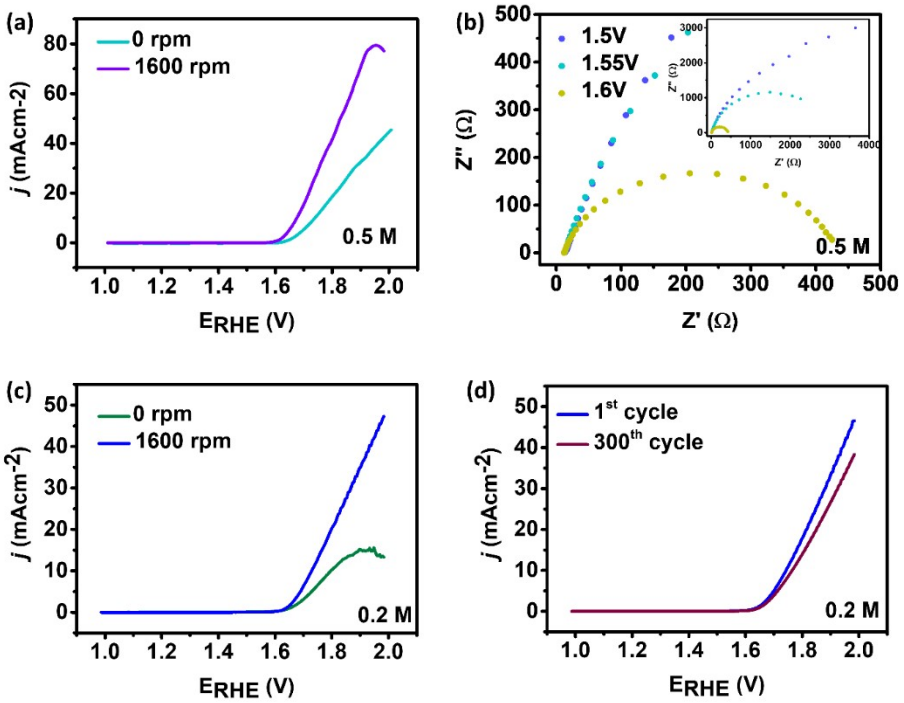


Fig S18. (a) LSV recorded at 5 mV s^{-1} in N_2 saturated 0.5 M KOH, (b) Nyquist plot in the frequency ranging from 0.1 to 10^5Hz in 0.5 M KOH, (c) LSV recorded at 5 mV s^{-1} in N_2 saturated 0.2 M KOH, and (d) LSV recorded for 300 cycles in N_2 saturated 0.2 M KOH

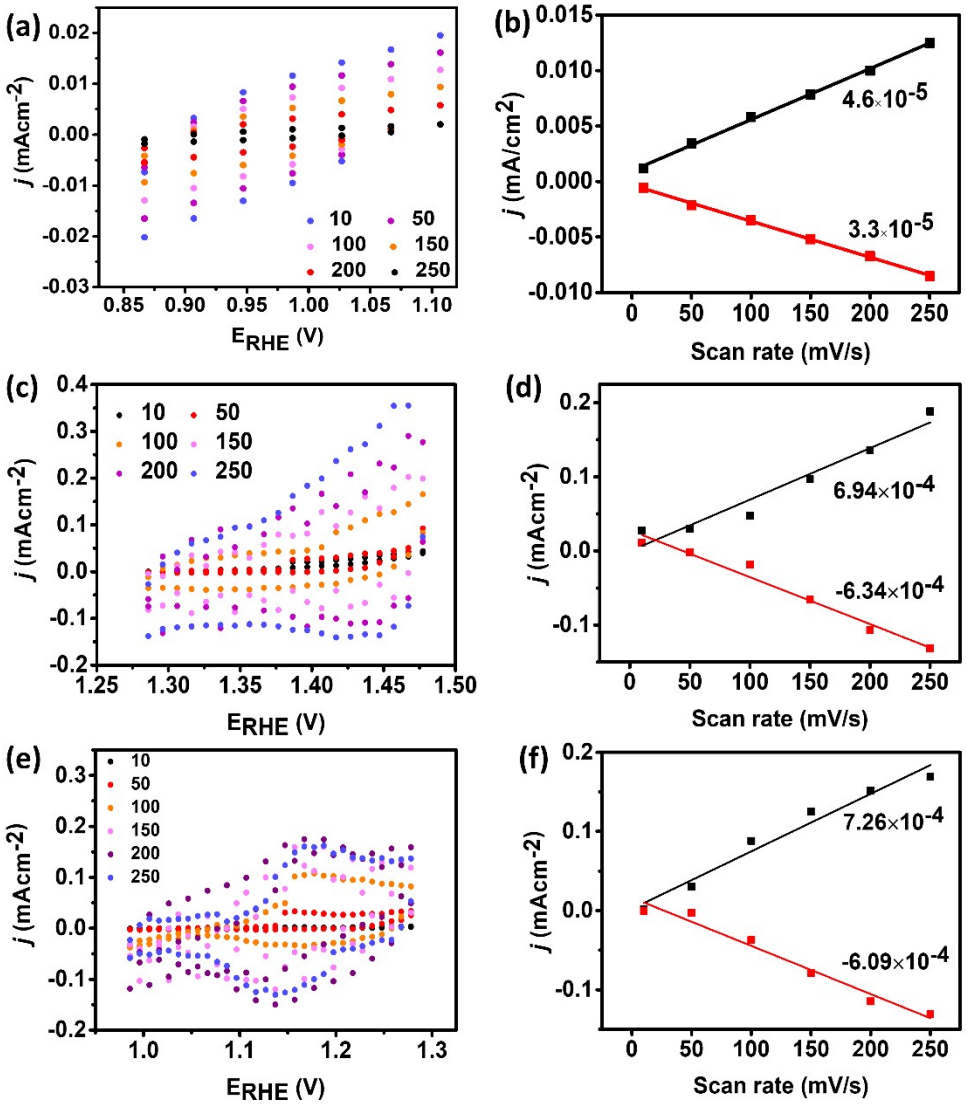


Fig S19. EASA for OER (a) Capacitance for bare GC, (b) corresponding *j* vs. scan rate plot for the capacitance of bare GC, (c) Capacitance for **TPA-tpd-Co**, (d) corresponding *j* vs. scan rate plot for the capacitance of **TPA-tpd-Co**, (e) cobalt peak for **TPA-tpd-Co**, and (f) corresponding *j* vs. scan rate plot for cobalt peak of **TPA-tpd-Co**

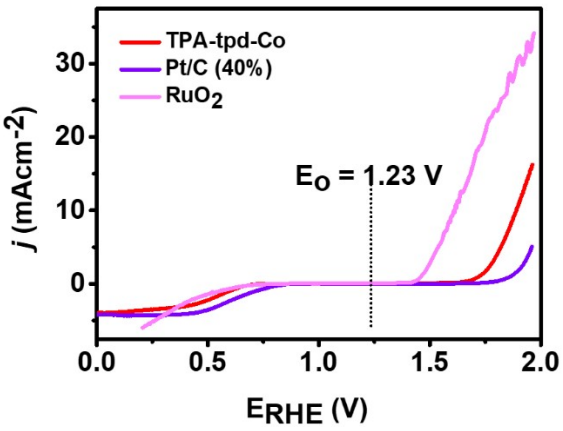


Fig S20. Overall bifunctional activity for as prepared **TPA-tpd-Co** along with precious metals (O_2 saturated 0.1M KOH, 1600 rpm, 5 m Vs^{-1})

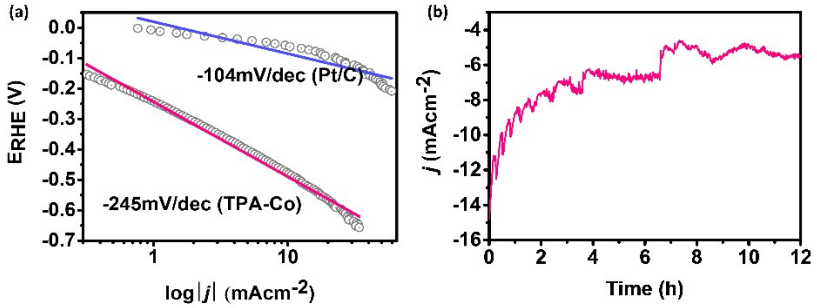


Fig S21. (a) Tafel plot recorded at 1 mV s^{-1} at 1600 rpm N_2 saturated 0.5M H_2SO_4, and (b) chronoamperometry at -0.48 V at 1600 rpm in N_2 saturated 0.5M H_2SO_4

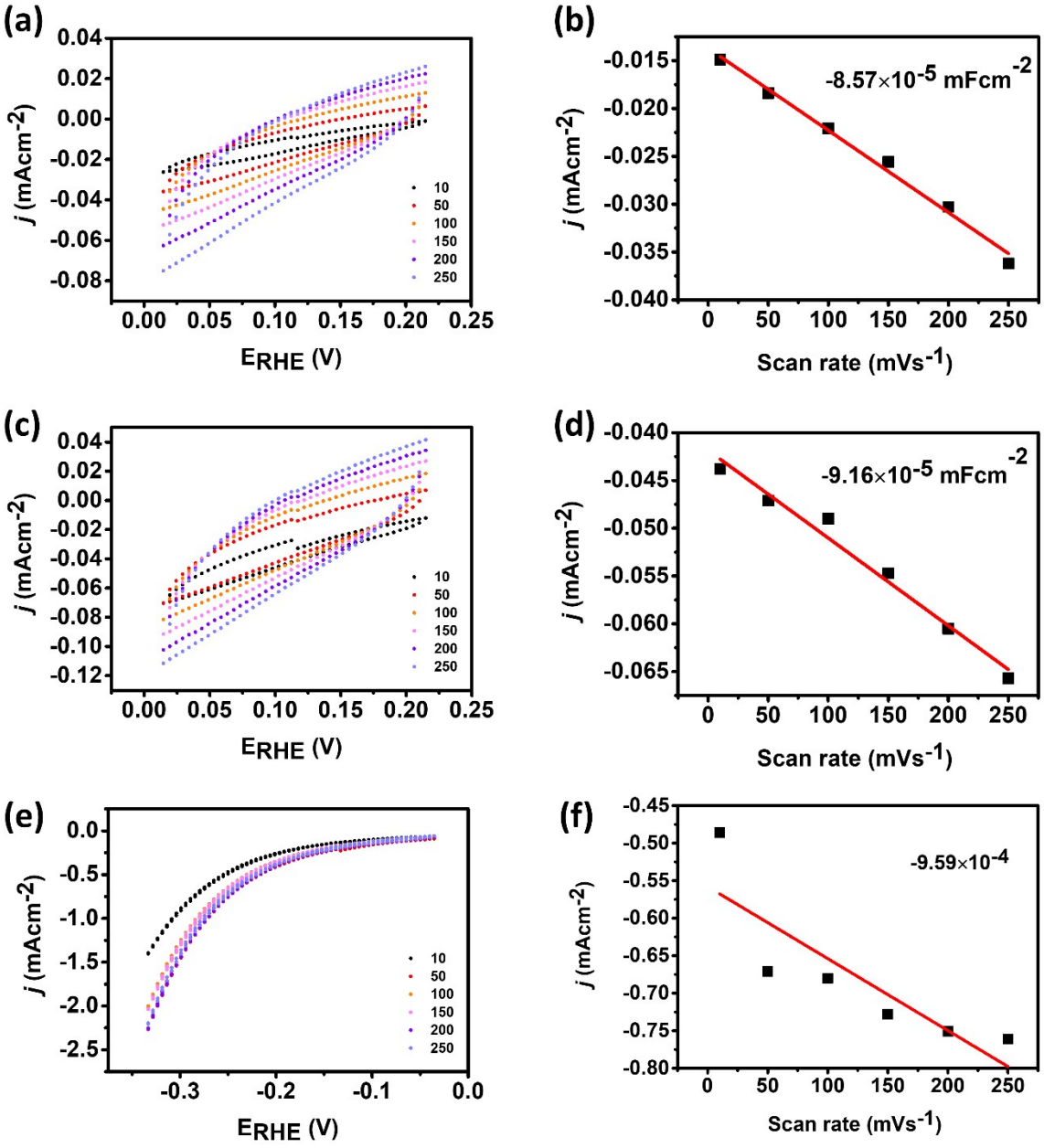


Fig S22. CV for EASA for HER (a) Capacitance for bare GC, (b) corresponding *j* vs. scan rate plot for the capacitance of bare GC, (c) Capacitance for **TPA-tpd-Co**, (d) corresponding *j* vs. scan rate plot for the capacitance of **TPA-tpd-Co**, (e) At the current onset region for **TPA-tpd-Co**, and (f) corresponding *j* vs. scan rate plot at the current onset region of **TPA-tpd-Co**

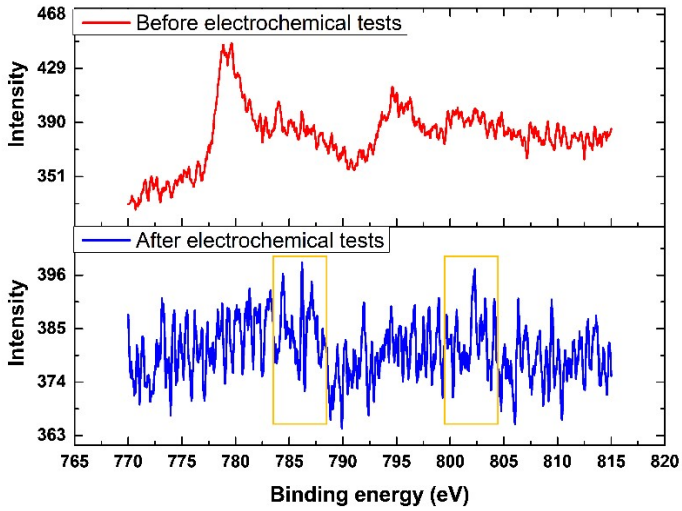


Fig S23. (a) Co2p XPS spectrum comparison before and after electrochemical stability tests

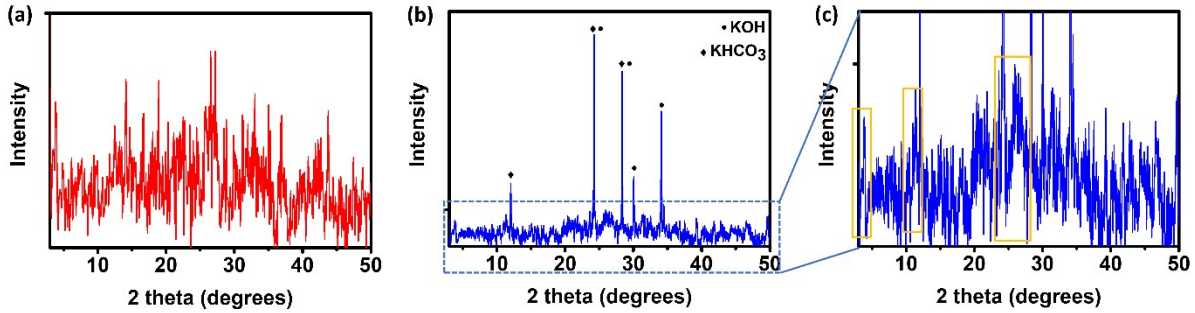


Fig S24 PXRD pattern of the electrocatalyst (a) before electrochemical stability test, (b) after electrochemical test, (c) enlarged section of PXRD pattern after electrochemical tests

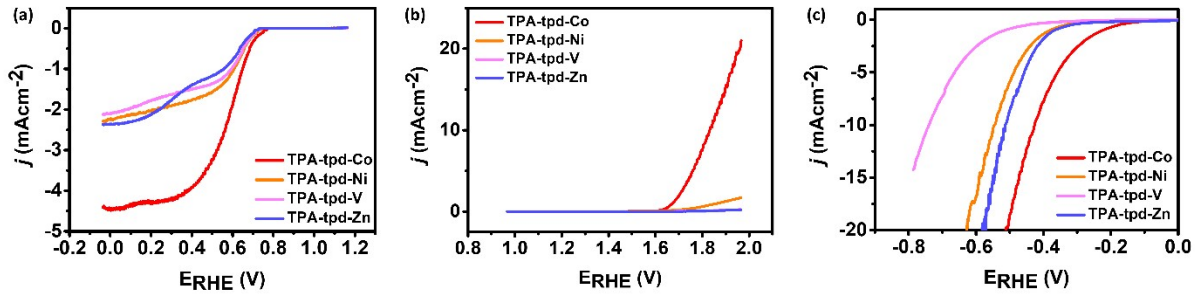


Fig S25. Material activity comparison towards (a) ORR; LSV in O_2 saturated 0.1M KOH in 1600 at scan rate 5 mV s^{-1}, (b) OER; LSV in N_2 saturated 0.1M KOH in 1600 at scan rate 5 mV s^{-1} and (c) HER; LSV in N_2 saturated 0.5M H_2SO_4 in 1600 at scan rate 5 mV s^{-1}

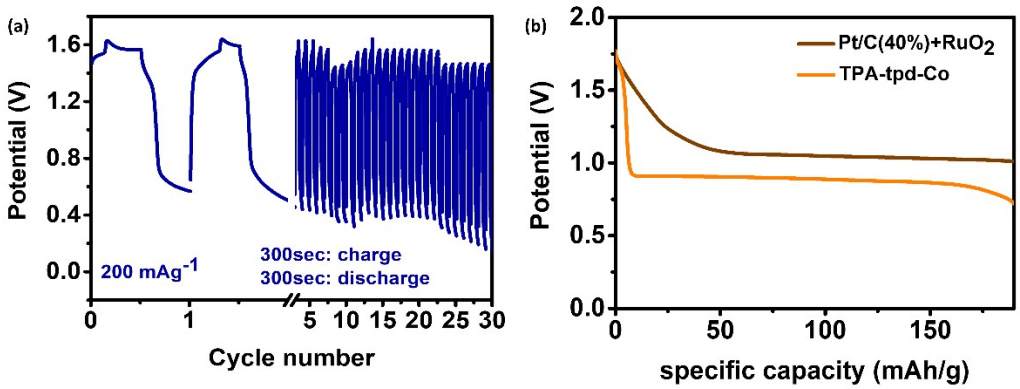


Fig S26. (a) Cyclic charge-discharge at 200 mA $g^{-1}_{TPA\text{-}tpd\text{-}Co}$, and (b) specific capacity comparison with the precious metals

Table S1: Electrocatalytic activity of several benchmark trifunctional metal-organic systems.

Catalyst	ORR				OER			HER			Ref
	Electrolyte	Loading (mg cm^{-2})	E_{onset} (V vs RHE)	n	Electrolyte	Loading (mg cm^{-2})	E_{onset} (V vs RHE)	Electrolyte	Loading (mg cm^{-2})	η_{-10} 1600 rpm (mV)	
TPA-tpd-Co	**0.1 M KOH**	**0.16**	**0.80**	**2.92-3.24**	**0.1 M KOH**	**0.16**	**1.6**	**0.5 M H_2SO_4**	**0.16**	**428**	**This work**
Defective graphene	0.1 M KOH	0.28	0.91	3.87	0.1 M KOH	0.28	1.6	0.5 M H_2SO_4	0.28	150	18
$FeCoNiO_x$@NG	1 M KOH	0.4	0.94	3.7-3.9	1 M KOH	0.4	1.51	1 M KOH	0.4	274	19
Ni-NC700	0.1 M KOH	0.31	0.88	~4	0.1 M KOH	0.31	1.52	0.1 M KOH	0.31	301	20
Fe_2P/Fe_4N@C-800	0.1 M KOH	0.3	0.89	4	1 M KOH	1.5	1.59	0.5 M H_2SO_4	1.5	232	21
Ni1Fe2-MOF	0.1 M KOH	0.25	0.80	4	0.1 M KOH	0.25	~1.4	0.1 M KOH	0.25	373	22
$CoFe/N_H$-C NS	0.1 M KOH	0.32	0.95	3.97	1 M KOH	0.32	1.5	1 M KOH	0.32	230	23
Co@IC/MoC@PC	0.1 M KOH	0.4	1.03	4	1 M KOH	0.4	1.5	1 M KOH	0.4	68	24
SHG	0.1 M KOH	0.64	1.01	3.85	0.1 M KOH	0.64	1.49	0.1 M KOH	0.64	300	25
W_2N/WC	0.1 M KOH	0.25	0.93	~4	0.1 M KOH	0.25	1.55	1 M KOH	0.25	145.5	26
Co/CNFs	0.1 M KOH	0.3	1.01	4	1 M KOH	0.3	1.5	1 M KOH	0.3	190	27

Co-N, P-HCS	0.1 M KOH	0.43	0.97		1 M KOH	0.43	~1.6	1 M KOH	0.43	164	28

Density functional theory computations

All computations were performed under the density functional theoretical (DFT) using the Gaussian 16[4]. The DFT computations were performed to evaluate the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and to better understand the reaction mechanistic of ORR, OER, and HER delivered by **TPA-tpd-Co**. The model structure of **TPA-tpd-Co** and adsorbed reaction intermediate configurations were optimized at B3LYP|6-31G** level (LanL2DZ: ECP and basis set of Co)[5-12]. Quadratic convergence (QC) was used for self-consistence field (SCRF) calculation because SCF convergence failed without QC. Grimme's GD3BJ empirical dispersion was also used to tackle weak interactions taking water as a solvent system using a polarizable continuum model (PCM). The orbital energy of **TPA-tpd-Co** was evaluated using the HSEH1PBE 6-31G** level of theory. All the structures were constructed using GaussView 6.0.16[13]. All the optimized configurations were subjected to harmonic frequency calculations to gain validation of stationary points and acquire thermochemistry information. The energy hindrances coming from the differences in free energy of reaction intermediates are considered for the study. The kinetic hindrances between the intermediates could also be participating but were not included. The adopted approach is to determine whether the intermediate one-electron transfer reaction is thermodynamically feasible or not, which is unambiguously the necessary condition (but not sufficient).

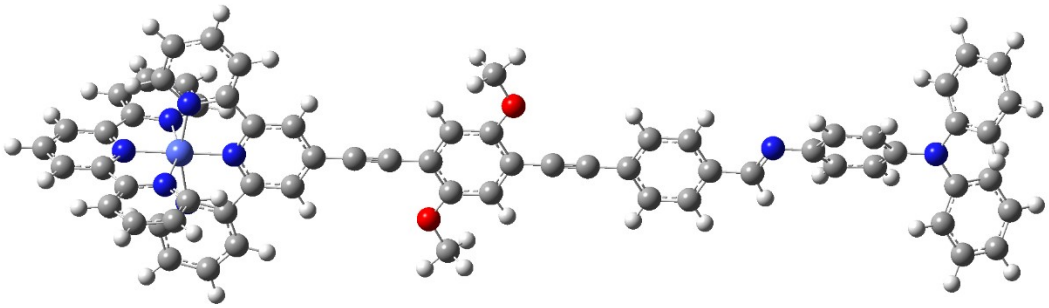


Fig S27. Optimized structure of **TPA-tpd-Co** obtained from DFT computation at B3LYP/6-31G** level (LANL2DZ: basis set and electron core potential of Co; solvent = water)

The electrocatalytic activity of **TPA-tpd-Co** towards ORR and OER was studied in alkaline media following an associative pathway.

ORR

The complete reduction reaction (ORR) cycle can be summarized in the following elementary steps

$$* + O_2(g) + H_2O\ (l) + e^- \rightarrow HOO^* + OH^- \quad (14)$$

$$HOO^* + e^- \rightarrow O^* + OH^- \quad (15)$$

$$O^* + H_2O\ (l) + e^- \rightarrow HO^* + OH^- \quad (16)$$

$$HO^* + e^- \rightarrow * + OH^- \quad (17)$$

Where, the * denotes the active adsorption site of the catalyst. (g) and (l) represent the gaseous and liquid phases.

The free energy of a reaction (ΔG) is given by the following equation

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} + \Delta G_{field} \quad (18)$$

Where, the ΔE is the energy change, ΔZPE is change in zero-point energy, ΔS is change in entropy, T is a temperature (298.15 K). $\Delta G_U = -eU$ is the change in electrode potential related to Standard Hydrogen Electrode. $\Delta G_{pH} = -kTln10.pH$ (pH=13) is the change in free energy accounting to the pH conditions. ΔG_{field} is the free energy correction accounting for electrochemical double layer and is neglected for this study. ΔE was determined the DFT computations while ΔZPE and $T\Delta S$ was taken from literatures[14, 15] and the free energy of OH^-, H_2O, and O_2 were determined accordingly.

OER

The complete oxidation reaction (OER) can be summarized in the following elementary steps

$$* + OH^- \rightarrow HO^* + e^- \quad (19)$$

$$HO^* + OH^- \rightarrow O^* + H_2O\,(l) + e^- \quad (20)$$

$$O^* + OH^- \rightarrow HOO^* + e^- \quad (21)$$

$$HOO^* + OH^- \rightarrow * + O_2(g) + H_2O(l) + e^- \quad (22)$$

The free energy was calculated as previously mentioned method.

Since it is challenging to determine the free energy of OOH, O and OH radicals in the media, the Gibbs free energy of the oxygenated reaction intermediates are described as follows

$$\Delta G_{OOH*} = G_{OOH*} + G_{H_2O} - G^* - 3G_{OH^-} \quad (23)$$

$$\Delta G_{O*} = G_{O*} + G_{H_2O} - G^* - 2G_{OH^-} \quad (24)$$

$$\Delta G_{OH*} = G_{OH*} - G^* - G_{OH^-} \quad (25)$$

Where * denotes the adsorption site on TPA-tpd-Co. The free energy valves are listed in Table S2

Table S2. The Gibbs adsorption energy (eV) of the oxygenated intermediates on TPA-tpd-Co for ORR and OER following equations 23, 24 and 25

Electrocatalytic reaction	ΔG_{OOH*} **(eV)**	ΔG_{O*} **(eV)**	ΔG_{OH*} **(eV)**
ORR	4.771945	4.667244	3.892054
OER	5.345591	4.458471	1.976015

HER

The HER reaction proceeds in two steps, (a) adsorption of the proton on the catalytic site ($H^+ + e^- + *$), and (b) release of dihydrogen molecule ($1/2H_2 + *$), where * is the active catalytic centre. The molecular hydrogen evolution reaction descriptor is the Gibbs free energy of the adsorbed proton (G_{H*}) and it should be closer to zero for optimum catalytic performance. The free energy is determined as

$$\Delta G_{H*} = E_{H*} - E_* - 0.5E_{H_2} + \Delta E_{ZPE} - T\Delta S \quad (26)$$

Where, the E_{H*} is the energy of catalyst with absorbed proton, E_{*} is the energy of catalyst, ΔE_{ZPE} is the difference between zero-point vibrational energy of gaseous hydrogen molecule and proton adsorbed catalyst. $E_{H_2}$is the energy of the hydrogen molecule[15-17]. The ΔG_{H*} is determined as

$$\Delta G_{H*} = E_{H*} - E_{*} - 0.5E_{H_2} + 0.24\ eV \quad (27)$$

Table S3. The values considered for calculation of free energy of reaction intermediates

		G (Ha)	E (Ha)	ZPE (Ha)	TS (Ha)
	*	-3314.892384	-3315.699884	0.990227805	0.18272812
ORR	HOO*	-3465.805126	-3466.621507	1.007137432	0.19075642
	O*	-3389.969344	-3390.775714	0.991736785	0.185367
	HO*	-3390.588976	-3391.418169	1.005799669	0.17660699
OER	HO*	-3390.659393	-3391.485501	1.006372488	0.18026456
	O*	-3389.977017	-3390.785494	0.992792195	0.18431506
	HOO*	-3465.784044	-3466.61489	1.010760578	0.17991438
HER	H*		-3316.203005		
	H_2O	-76.43077263	-76.42673	0.020580669	0.0246233 (0.035 bar)
	H_2	-1.182285167	-1.17714	0.009922822	0.01506799
	0.5 O_2	-75.13823313	-75.14815595	0.00183756	0.011760382

XYZ coordinates

TPA-tpd-Co

Charge 2, multiplicity 2

H,17.0003687596,-4.9092704164,1.3192652395
H,19.0169206244,-5.2003253341,-0.1123796813
N,10.8678299268,-0.2671236369,0.0842525204
C,10.1256457763,-1.3073829216,-0.0573750134
H,10.5467751037,-2.3166286387,-0.1537581787
C,8.6661101494,-1.22747437,-0.0798113361
C,7.9911864367,0.0034901843,0.0309933044
C,7.9130800754,-2.406619579,-0.213112443
C,6.6079319653,0.0528793709,0.0124743696
H,8.576546673,0.9103793168,0.1327994006
C,6.5254880354,-2.3665619872,-0.2344157524
H,8.426066611,-3.3601281179,-0.300231498
C,5.8504113201,-1.1339967076,-0.1211017519
H,6.090139184,1.0020900696,0.0994073926
H,5.9504277128,-3.2802499628,-0.3373755608
C,4.4327364948,-1.0808472638,-0.1388297631
C,3.2167445093,-1.0247599632,-0.1505688519
C,1.8018441932,-0.9759586331,-0.1630007079
C,1.1306791659,0.2715796373,-0.0598024594
C,1.0554904756,-2.1636112973,-0.2759950635
C,-0.2584328281,0.3007604119,-0.070906226
C,-0.3365959586,-2.1362350733,-0.2871115452
H,1.595029405,-3.0976788914,-0.3530337388
C,-1.0054034968,-0.8899397556,-0.1829419136
H,-0.7985438487,1.2345567837,0.00656594
C,-2.4173894511,-0.8395965848,-0.189509672
C,-3.6332756513,-0.7824913746,-0.1925494364
C,-5.0445555347,-0.7253983122,-0.1944857186
C,-5.7127052714,0.5140565158,-0.0973179035
C,-5.807482843,-1.9090814099,-0.2930425178
C,-7.1010756865,0.5326527133,-0.1003621765
H,-5.1395160509,1.4283792634,-0.0225321913
C,-7.1931363513,-1.8189932729,-0.2905288197
H,-5.3063730397,-2.86494449,-0.3686244766
C,-8.1528481132,-2.9345884604,-0.3839502922
C,-7.7974631085,-4.2769025992,-0.4875267801
C,-8.805290032,-5.2367642793,-0.5686170221
H,-6.7550416936,-4.5691586087,-0.5046085128
C,-10.4191635324,-3.4683050734,-0.4374614001
C,-10.1367518498,-4.828568674,-0.5433748358
H,-8.5504912424,-6.2874275997,-0.649901316
H,-11.4392976307,-3.1045690806,-0.4134605231
H,-10.9485649062,-5.5432771601,-0.6037915099
C,-7.9696898414,1.7204317741,-0.0078173186
C,-7.5082992607,3.0294500158,0.1043644515
C,-10.1858400397,2.433566897,0.0371214245
C,-8.4362292382,4.0667739498,0.1846791107

H,-6.4457783314,3.2370148783,0.1293845885
C,-9.7959278661,3.7663822809,0.1505560081
H,-11.2319937354,2.1538405565,0.0069126786
H,-8.0985925236,5.0932518016,0.2726823847
H,-10.5485442039,4.5432526652,0.2102726637
N,-7.7991295894,-0.6175057082,-0.1954364867
N,-9.2992342966,1.4349638744,-0.0400671177
N,-9.4555428682,-2.5438704066,-0.3599370585
C,-9.6768658964,-0.5432513037,-0.2030227536
C,-12.2587486459,-0.351371333,-1.3967837412
C,-13.6533755729,-0.295159785,-1.4334295584
C,-14.3617063263,-0.3631070716,-0.236975401
C,-13.6784482597,-0.485690021,0.9696678237
C,-12.283204149,-0.5373637009,0.9538230166
H,-14.1792862032,-0.2000709718,-2.3738172606
H,-15.444850331,-0.3209405817,-0.2448771089
H,-14.2241493664,-0.5392920604,1.9020183064
N,-11.6111411223,-0.4689780331,-0.2165358867
C,-11.4391359692,-0.6663663531,2.1649714519
C,-11.9560560794,-0.7509694062,3.4597195263
C,-9.2635683852,-0.8121020213,2.9608110456
C,-11.0708197511,-0.8702868748,4.5297648969
H,-13.0233675291,-0.7252859823,3.6382689645
C,-9.7000071993,-0.9019469541,4.2819129198
H,-8.2069455806,-0.8318211357,2.7127880423
H,-11.4510212894,-0.937463552,5.5430928765
H,-8.9812068037,-0.9937562828,5.0875647731
C,-11.3897801517,-0.2911599454,-2.5955173999
C,-11.8797520642,-0.1753632815,-3.898242521
C,-10.9722732792,-0.1271077773,-4.9551612495
H,-12.9433335796,-0.1238984696,-4.092818984
C,-9.1977617303,-0.3107050877,-3.3587584295
C,-9.6066680958,-0.1952777901,-4.6866575764
H,-11.3313440964,-0.0374021468,-5.974435894
H,-8.1464813346,-0.3676363475,-3.0943815644
H,-8.871179279,-0.1606393842,-5.4816636703
N,-10.109216297,-0.6978863427,1.9344972732
N,-10.0648034805,-0.3573111932,-2.3451306492
O,1.92558861,1.3673465889,0.0449032414
O,-1.127956884,-3.2319405871,-0.391654968
C,1.2948256575,2.6422934823,0.1505801859
H,0.6696160323,2.7027489734,1.0484619359
H,2.1032609606,3.3695106806,0.2207822449
H,0.6847154752,2.8578503963,-0.7337243403
C,-0.4977337548,-4.5085239672,-0.4971172051
H,0.1266385589,-4.5688944509,-1.395152895
H,0.1115760047,-4.7235215495,0.3874327669

H,-1.3075285925,-5.2341082308,-0.5669719035

ORR reaction intermediates

HOO* (TPA-tpd-Co-OOH)

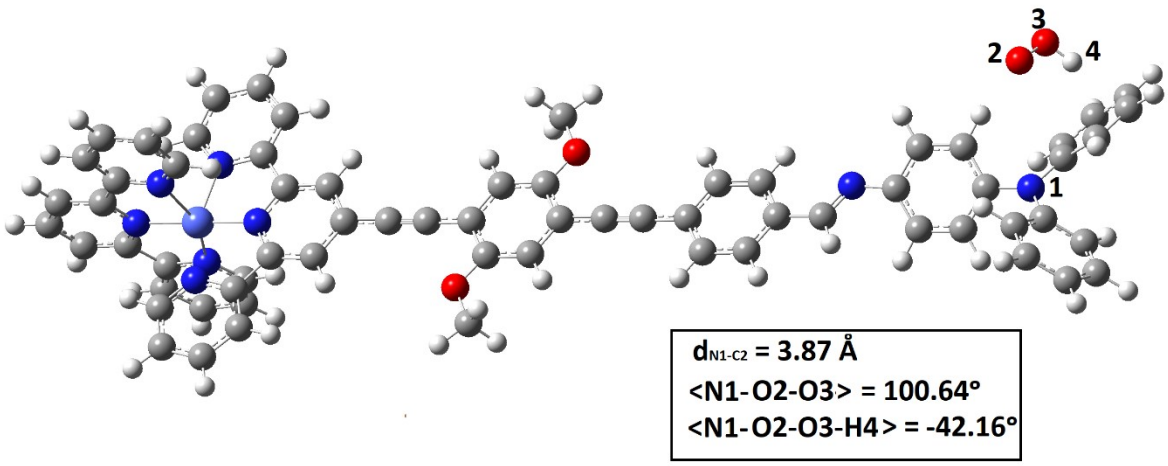


Fig S28. Optimized structure of **TPA-tpd-Co-OOH** obtained from DFT computation at B3LYP/6-31G** level (LANL2DZ: basis set and electron core potential of Co; solvent = water)

XYZ coordinates

Charge 2, multiplicity 1

N -16.05243600 0.14066800 -0.24987900
C -14.63826100 0.07161200 -0.21483400
C -13.86614700 1.07613000 -0.82035900
C -13.98754800 -1.00141000 0.41475700
C -12.47922700 1.02417800 -0.77691000
H -14.36352400 1.89183000 -1.33352100
C -12.60083100 -1.06788200 0.42567100
H -14.57463600 -1.77760000 0.89132300
C -11.81978600 -0.04632500 -0.14230400
H -11.90239800 1.79318900 -1.28036100
H -12.09483800 -1.89864500 0.90672200
C -16.81910200 -1.01542700 -0.50805800
C -18.04946000 -1.21293400 0.14246000
C -16.36340600 -1.98951400 -1.41151800
C -18.80577500 -2.35782600 -0.11710400
H -18.40418800 -0.47465000 0.85165100
C -17.11571900 -3.13722700 -1.65154400
H -15.41633900 -1.84364900 -1.91806500

C -18.34398400 -3.33087200 -1.01355000
H -19.75551600 -2.49271600 0.39122000
H -16.74378400 -3.87914800 -2.35103900
H -18.93069500 -4.22286800 -1.20422500
C -16.69439100 1.38966700 -0.03472200
C -17.77040500 1.78408400 -0.84292700
C -16.24961400 2.24219600 0.98584000
C -18.39729400 3.00896400 -0.62185900
H -18.10917000 1.12882700 -1.63801500
C -16.86992600 3.47377800 1.18703400
H -15.42044600 1.93403400 1.61329500
C -17.94916400 3.86254800 0.38943600
H -19.23002000 3.30271400 -1.25366300
H -16.51609900 4.12524800 1.98032400
H -18.43479900 4.81908300 0.55361300
N -10.42585700 -0.18311000 -0.07753100
C -9.67440300 0.85907100 -0.04156500
H -10.08763600 1.87522800 0.00236900
C -8.21515100 0.76910100 -0.03752500
C -7.55171300 -0.47202700 -0.08448800
C -7.45183200 1.94782900 0.01450100
C -6.16882000 -0.53208000 -0.07734400
H -8.14544400 -1.37828700 -0.12477800
C -6.06433200 1.89737600 0.01913200
H -7.95629800 2.90914200 0.05021000
C -5.40064500 0.65440100 -0.02651800
H -5.65940600 -1.48909600 -0.11231700
H -5.48088300 2.81067600 0.05826900
C -3.98334300 0.58909500 -0.02222200
C -2.76805100 0.51931700 -0.01953900
C -1.35390300 0.45138500 -0.01678300
C -0.70169400 -0.81024900 -0.03771800
C -0.58990000 1.63289200 0.00639800
C 0.68691600 -0.85920800 -0.03469400
C 0.80172000 1.58568900 0.00861800
H -1.11544200 2.57792100 0.02206700
C 1.45160300 0.32524700 -0.01197100
H 1.21304300 -1.80401400 -0.05003000
C 2.86270500 0.25467300 -0.00977300
C 4.07766700 0.18054900 -0.00794200
C 5.48801600 0.10436400 -0.00536700
C 6.13898600 -1.14800800 -0.00469200
C 6.26682600 1.28181800 -0.00325100
C 7.52679800 -1.18516700 -0.00158700
H 5.55314100 -2.05730200 -0.00621500
C 7.65102800 1.17318400 -0.00086700
H 5.77849700 2.24720400 -0.00378400

C 8.62619000 2.27998400 0.00075500
C 8.28982700 3.63096600 0.00007000
C 9.31081900 4.58041800 0.00167400
H 7.25155000 3.93808500 -0.00170700
C 10.90105400 2.78608600 0.00444000
C 10.63670700 4.15399000 0.00389400
H 9.07003300 5.63750600 0.00116100
H 11.91571600 2.40693800 0.00612000
H 11.45804200 4.86026100 0.00517900
C 8.37967500 -2.38845600 0.00060100
C 7.90137300 -3.69594500 -0.00009700
C 10.58740400 -3.13324900 0.00626600
C 8.81543000 -4.74872200 0.00251600
H 6.83615500 -3.89078200 -0.00255700
C 10.17910100 -4.46529900 0.00576900
H 11.63687000 -2.86511500 0.00866600
H 8.46375900 -5.77424900 0.00204900
H 10.92108400 -5.25454300 0.00790400
N 8.24074300 -0.04040900 0.00004700
N 9.71398300 -2.12000300 0.00377500
N 9.92456200 1.87176000 0.00288300
Co 10.12388100 -0.13942400 0.00375000
C 12.74552800 -0.26859900 -1.17027700
C 14.14052600 -0.33171400 -1.19229700
C 14.83499700 -0.36214100 0.01263200
C 14.13612700 -0.32898900 1.21494500
C 12.74122400 -0.26579500 1.18771400
H 14.67892800 -0.35613300 -2.12978600
H 15.91789100 -0.41086500 0.01467500
H 14.67108800 -0.35152000 2.15444600
N 12.07940800 -0.23745100 0.00747000
C 11.90078500 -0.22480200 2.41048400
C 12.42875800 -0.24984100 3.70440100
C 9.73379500 -0.11903300 3.23795800
C 11.55409500 -0.20658000 4.78863200
H 13.49632500 -0.30198800 3.87366200
C 10.18152700 -0.13982500 4.55815200
H 8.67563900 -0.06800200 3.00067800
H 11.94445200 -0.22500900 5.80018300
H 9.47107700 -0.10467900 5.37560500
C 11.90956800 -0.23062500 -2.39619800
C 12.44218100 -0.26118100 -3.68808300
C 11.57150700 -0.22070800 -4.77562800
H 13.51026400 -0.31566600 -3.85325300
C 9.74573800 -0.12489900 -3.23189600
C 10.19821200 -0.15117200 -4.55037800
H 11.96550400 -0.24351800 -5.78567500

H 8.68680100 -0.07162100 -2.99864400
H 9.49079100 -0.11810600 -5.37053900
N 10.57035900 -0.16037600 2.19920000
N 10.57847700 -0.16357400 -2.18996200
O -1.51312800 -1.89858100 -0.05945500
O 1.60965100 2.67400800 0.02972900
C -0.90175700 -3.18716800 -0.07949600
H -0.28797400 -3.34924100 0.81363900
H -1.72120100 -3.90526100 -0.09291600
H -0.28452400 -3.31985600 -0.97511500
C 0.99888300 3.96421000 0.04954700
H 0.38542400 4.12557800 -0.84350500
H 0.38294500 4.09697700 0.94561400
H 1.81967700 4.68062100 0.06219200
O -16.22279100 -2.57543400 2.50481400
O -16.64270700 -3.61863000 1.79559200
H -17.34336800 -3.25936000 1.19566600

O* (TPA-tpd-Co-O)

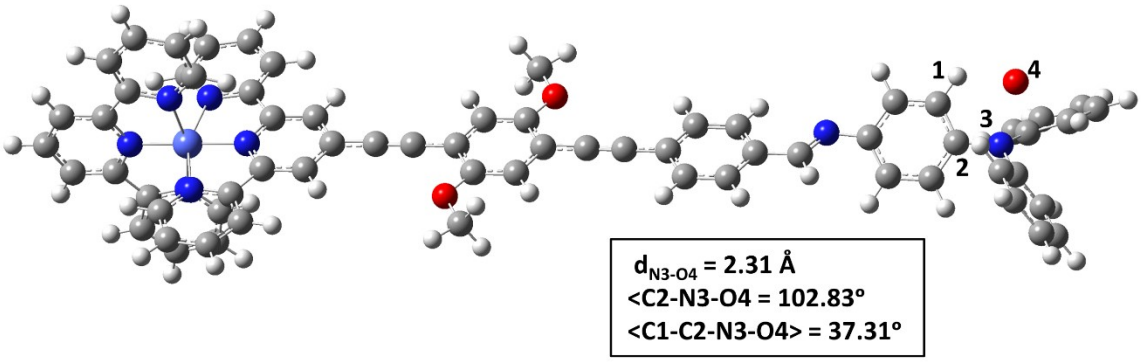


Fig S29. Optimized structure of **TPA-tpd-Co-O** obtained from DFT computation at B3LYP/6-31G** level (LANL2DZ: basis set and electron core potential of Co; solvent = water)

XYZ coordinates

Charge 2, multiplicity 2

N -16.28209100 -0.16484100 0.09576500
C -14.85423300 -0.20213500 0.15029300
C -14.08940600 0.67725100 -0.62599900
C -14.21212700 -1.14833100 0.96167900
C -12.70018600 0.62671200 -0.57743700

H -14.58362500 1.38910800 -1.27705200
C -12.82695800 -1.21514700 0.98570800
H -14.81825800 -1.80220000 1.57567400
C -12.04644100 -0.31359000 0.23883500
H -12.11953800 1.29059600 -1.20923600
H -12.32135700 -1.94529800 1.60897900
C -16.99155600 -1.33370400 -0.30447600
C -18.34047000 -1.47016800 0.06401400
C -16.36894400 -2.34454700 -1.04743200
C -19.05006900 -2.60892500 -0.30773900
H -18.81347400 -0.68538200 0.64105800
C -17.08883900 -3.48337400 -1.40736300
H -15.33236400 -2.23819200 -1.34306200
C -18.42933400 -3.62303200 -1.04202400
H -20.09093600 -2.70605800 -0.01523500
H -16.59796600 -4.25998600 -1.98564000
H -18.98452900 -4.51071700 -1.32722700
C -16.89222200 1.11337800 -0.10928100
C -17.70494100 1.35441100 -1.22176300
C -16.63380300 2.13993300 0.80663000
C -18.26342800 2.61979800 -1.40858600
H -17.89336800 0.55934500 -1.93393300
C -17.18436400 3.40230000 0.60577300
H -16.01325100 1.93134000 1.67066600
C -18.00449200 3.64732600 -0.50053800
H -18.89334000 2.80158400 -2.27371300
H -16.98410900 4.19351600 1.32143700
H -18.43893800 4.63049000 -0.65024300
N -10.65189400 -0.43698000 0.31864400
C -9.91093400 0.60912200 0.23129400
H -10.33718900 1.61845000 0.15995100
C -8.45075800 0.53654500 0.23799500
C -7.77350700 -0.69428700 0.32981100
C -7.70249600 1.72237700 0.14887900
C -6.38992400 -0.73733800 0.33330800
H -8.35635700 -1.60587900 0.39873600
C -6.31449300 1.68858200 0.14880600
H -8.21866300 2.67541500 0.07774100
C -5.63646100 0.45600300 0.24097000
H -5.86898800 -1.68601500 0.40479500
H -5.74182100 2.60672200 0.07812600
C -4.21839800 0.40826500 0.23951100
C -3.00236100 0.35505200 0.23648800
C -1.58733400 0.30760100 0.22690500
C -0.91601900 -0.93831900 0.34506000
C -0.84189000 1.49402100 0.09719500
C 0.47321700 -0.96767100 0.32795700

C 0.55011200 1.46639300 0.08012600
H -1.38170800 2.42698400 0.00962900
C 1.21920800 0.22126000 0.19562200
H 1.01350300 -1.90058800 0.41411900
C 2.63129200 0.17113900 0.17324200
C 3.84692900 0.11643800 0.15065300
C 5.25835800 0.06501500 0.11340400
C 5.93936900 -1.16324600 0.20970200
C 6.01536200 1.24383400 -0.02637700
C 7.32849800 -1.17986000 0.15924400
H 5.37229300 -2.07722700 0.31810900
C 7.40242000 1.16397600 -0.06853400
H 5.50671200 2.19466800 -0.10313900
C 8.29530400 2.33892400 -0.21425100
C 7.83317300 3.65413700 -0.29955700
C 8.76165900 4.68477300 -0.43481100
H 6.77496100 3.87876400 -0.26062800
C 10.50095300 3.04057700 -0.38789200
C 10.12025800 4.37845200 -0.48076600
H 8.42432300 5.71313100 -0.50262000
H 11.54574900 2.74756800 -0.41719100
H 10.87148900 5.15234000 -0.58516500
C 8.14548800 -2.41465400 0.24256500
C 7.60164400 -3.69245900 0.39115500
C 10.30259900 -3.27153900 0.22361800
C 8.46350200 -4.78589400 0.45607800
H 6.53142100 -3.84076500 0.45578800
C 9.83869500 -4.57786500 0.37105300
H 11.36358500 -3.05376800 0.15194500
H 8.06181500 -5.78651100 0.57134800
H 10.53971500 -5.40285500 0.41704800
N 8.03021300 -0.03126500 0.02137500
N 9.47920700 -2.22269300 0.16197900
N 9.61354300 2.05178400 -0.25851100
Co 9.96077400 -0.10083000 -0.06976700
C 12.42167000 -0.31698600 -1.37030900
C 13.81198300 -0.37625000 -1.47003000
C 14.56775500 -0.28081100 -0.30113300
C 13.94234600 -0.12912500 0.93678100
C 12.54894500 -0.07566500 0.97689100
H 14.29616300 -0.49436300 -2.43092200
H 15.64942400 -0.32506600 -0.35503700
H 14.52772800 -0.05570300 1.84415100
N 11.83933800 -0.17103600 -0.16429100
C 11.69628000 0.07869100 2.16915000
C 12.17374600 0.20702300 3.47113600
C 9.48960300 0.22280200 2.90020100

C 11.25895400 0.34677700 4.51396600
H 13.23842000 0.19969800 3.66894500
C 9.89618200 0.35457200 4.22644000
H 8.44069700 0.22475200 2.62987100
H 11.60927700 0.44822500 5.53493500
H 9.15374900 0.46096100 5.00807600
C 11.44486600 -0.39788400 -2.47090400
C 11.77918000 -0.54888900 -3.81429000
C 10.75714300 -0.61348400 -4.76037900
H 12.81652500 -0.61492100 -4.11756400
C 9.17169600 -0.37393000 -2.97755000
C 9.43292800 -0.52515100 -4.33784600
H 10.99559700 -0.73080000 -5.81146600
H 8.15781100 -0.30048900 -2.60329400
H 8.61049100 -0.57114200 -5.04138400
N 10.36341200 0.08863800 1.89668200
N 10.14884100 -0.31150300 -2.06647500
O -1.71049500 -2.03231600 0.46768000
O 1.34113000 2.56042100 -0.04253000
C -1.07921400 -3.30554400 0.59095200
H -0.45120100 -3.35188800 1.48768900
H -1.88735100 -4.03161100 0.67490600
H -0.47188000 -3.53460200 -0.29181800
C 0.71026800 3.83511100 -0.16586200
H 0.08326200 3.88129900 -1.06290800
H 0.10346500 4.06363800 0.71699100
H 1.51965300 4.55970900 -0.24927900
O -16.89168400 -0.63575500 2.27469900

HO* (TPA-tpd-Co-OH)

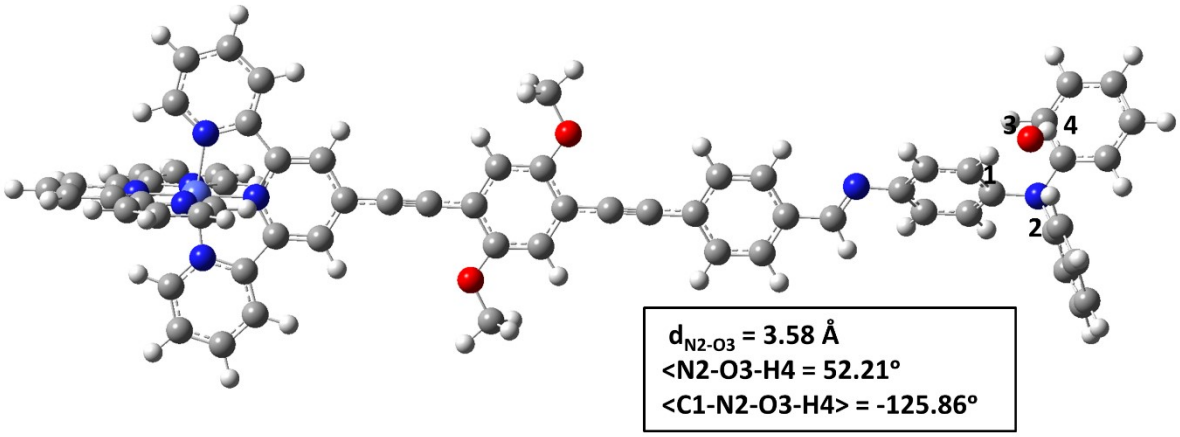


Fig S30. Optimized structure of **TPA-tpd-Co-OH** obtained from DFT computation at B3LYP/6-31G** level (LANL2DZ: basis set and electron core potential of Co; solvent = water)

XYZ coordinates

Charge 2, multiplicity 1

N -16.23542600 0.00606500 -0.42416500
C -14.80112800 -0.08219100 -0.32900200
C -14.02009700 0.47750100 -1.34321800
C -14.20100500 -0.71228000 0.77197200
C -12.62936200 0.43394100 -1.26465700
H -14.50913800 0.93740500 -2.19652000
C -12.81152600 -0.77556700 0.82775800
H -14.85401700 -1.12536400 1.57808100
C -12.00864900 -0.18836800 -0.16738700
H -12.02557500 0.84313900 -2.06846400
H -12.31285200 -1.26193000 1.66235300
C -16.99172900 -1.15461500 -0.60118500
C -18.38860400 -1.14937100 -0.40432200
C -16.38946000 -2.35008300 -1.04699300
C -19.14156300 -2.29863000 -0.63471800
H -18.87639500 -0.24305800 -0.06708300
C -17.15690500 -3.49028900 -1.27165800
H -15.31922100 -2.37855200 -1.21176200
C -18.53925400 -3.48220500 -1.06809700
H -20.21528200 -2.26386100 -0.47028200
H -16.66288600 -4.39676700 -1.61131300
H -19.13129200 -4.37490900 -1.24249700
C -16.81383600 1.13933500 0.25526300
C -17.11323000 2.28884100 -0.47931900
C -17.04520100 1.08376800 1.63634900
C -17.64597300 3.40736200 0.16677000
H -16.92671000 2.29814100 -1.54894200
C -17.58343900 2.20798400 2.26695000
H -16.78789800 0.15050300 2.18406400
C -17.88256100 3.36696400 1.54243800
H -17.87680000 4.30300700 -0.40255400
H -17.76954500 2.18426700 3.33830400
H -18.29829100 4.23474400 2.04703200
N -10.61283500 -0.29494700 -0.03335500
C -9.86157700 0.67337200 -0.41495400
H -10.27762900 1.61749600 -0.79092500
C -8.40071400 0.59849600 -0.36200800
C -7.73823400 -0.56524700 0.07179300
C -7.63893200 1.71153200 -0.75461100
C -6.35527700 -0.61446800 0.11126000

H -8.33253800 -1.42046000 0.37342300
C -6.25141600 1.67229200 -0.71675300
H -8.14377800 2.61248000 -1.09114800
C -5.58841400 0.50609700 -0.28376000
H -5.84538900 -1.51201600 0.44430100
H -5.66789700 2.53441300 -1.02047000
C -4.17119000 0.45189700 -0.24540600
C -2.95582700 0.39340500 -0.21070900
C -1.54242600 0.33758800 -0.17575800
C -0.88747300 -0.88598000 0.13516000
C -0.78362700 1.48970500 -0.44944700
C 0.49956600 -0.92699500 0.16191000
C 0.60826200 1.45261300 -0.41997800
H -1.31194400 2.40410100 -0.68194700
C 1.26074600 0.23003000 -0.11178800
H 1.02856800 -1.84161600 0.39250500
C 2.66777900 0.17190700 -0.07969200
C 3.88471400 0.11314700 -0.05036600
C 5.28893900 0.05911000 -0.02037200
C 5.95593700 -1.16387400 0.23605600
C 6.05242300 1.23040000 -0.24875200
C 7.34111900 -1.17926800 0.25515600
H 5.38164800 -2.06350800 0.41098100
C 7.43448000 1.14567800 -0.21104500
H 5.55109400 2.16795700 -0.44750400
C 8.41858100 2.21832800 -0.41466500
C 8.10883400 3.54698200 -0.67736500
C 9.14671900 4.46213200 -0.85053900
H 7.07491700 3.86105400 -0.74351400
C 10.71250300 2.68042900 -0.48975100
C 10.46467000 4.02415800 -0.75627200
H 8.92417800 5.50278100 -1.05570900
H 11.72230400 2.30236600 -0.40885000
H 11.29876000 4.70253800 -0.88446400
C 8.23723700 -2.32079900 0.48921000
C 7.82371000 -3.62322300 0.74054400
C 10.48779700 -2.94875900 0.63481200
C 8.78625900 -4.61162200 0.94389300
H 6.76815400 -3.86129900 0.77569300
C 10.13475700 -4.27074700 0.89131600
H 11.52451300 -2.64559100 0.58661400
H 8.48209100 -5.63312200 1.14038300
H 10.91294300 -5.00785100 1.04437300
N 8.02671800 -0.03969600 0.03554800
N 9.56338500 -2.00109700 0.43822500
N 9.71561100 1.80292000 -0.32344600
Co 9.89007200 -0.10833800 0.06040800

C 12.39581600 -0.43406500 -1.07388400
C 13.78843700 -0.49239700 -1.08587800
C 14.46960300 -0.27925800 0.11484200
C 13.77775700 -0.01544100 1.29935500
C 12.38546100 0.03126000 1.25422500
H 14.33056200 -0.69619500 -1.99992600
H 15.55237200 -0.31966200 0.12774900
H 14.31167000 0.14885300 2.22606900
N 11.75944300 -0.17771100 0.08258400
C 11.43959100 0.28738300 2.34930600
C 11.79558600 0.53478400 3.66922300
C 9.16511300 0.48641900 2.86577000
C 10.79054000 0.76382300 4.60903800
H 12.83868300 0.54768300 3.95861500
C 9.45965200 0.74020100 4.20307000
H 8.14374300 0.46054500 2.51183700
H 11.04906700 0.95772400 5.64350300
H 8.65039600 0.91382400 4.90111600
C 11.46010600 -0.62054400 -2.19147200
C 11.82882100 -0.89712300 -3.50208600
C 10.83280300 -1.05209400 -4.46633400
H 12.87482700 -0.98983100 -3.76517700
C 9.19056500 -0.64862200 -2.76377100
C 9.49794900 -0.92678400 -4.09332700
H 11.10126000 -1.26772300 -5.49395900
H 8.16543700 -0.54396100 -2.43609000
H 8.69522800 -1.04012800 -4.81106400
N 10.12981000 0.26518000 1.96566900
N 10.14669000 -0.49972200 -1.83983100
O -1.69848200 -1.94426100 0.38551800
O 1.41241500 2.51195900 -0.66835600
C -1.08674200 -3.19491200 0.69791100
H -0.48127500 -3.12365200 1.60836700
H -1.90609600 -3.89465600 0.85951100
H -0.46172500 -3.54777100 -0.12998900
C 0.80074900 3.76524000 -0.97929600
H 0.19831900 3.69501000 -1.89117600
H 0.17518400 4.11490400 -0.15120200
H 1.62180900 4.46359300 -1.13707600
O -16.21356900 -1.58155500 2.79135900
H -16.68145500 -1.86569500 1.99243400

OER reaction intermediates

HO* (TPA-tpd-Co-OH)

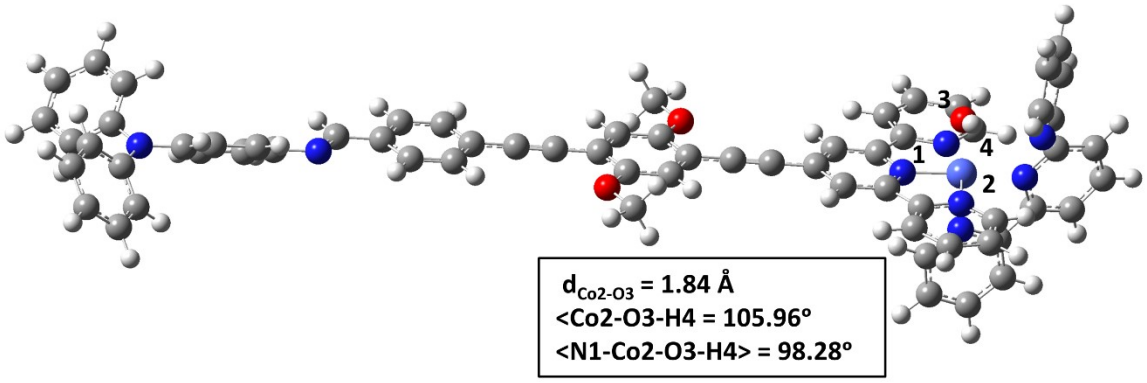


Fig S31. Optimized structure of **TPA-tpd-Co-OH** obtained from DFT computation at B3LYP/6-31G** level (LANL2DZ: basis set and electron core potential of Co; solvent = water)

XYZ coordinates

Charge 2, multiplicity 1

N -16.76346500 0.20112500 -0.01471100
C -15.35266200 0.23509700 -0.03073200
C -14.60557300 -0.83118400 0.50091100
C -14.66626300 1.34164000 -0.55974600
C -13.21812500 -0.80642500 0.47658300
H -15.12363300 -1.67438600 0.94379200
C -13.27878700 1.37743600 -0.55079400
H -15.22823700 2.17394400 -0.96786100
C -12.52558400 0.29577700 -0.06200200
H -12.66600900 -1.62650800 0.92421900
H -12.74989900 2.23460300 -0.95481300
C -17.50466500 1.38726700 0.22763300
C -18.65460000 1.66792300 -0.52502400
C -17.09886500 2.28728900 1.22419800
C -19.38782500 2.82664400 -0.27652700
H -18.96716400 0.97475800 -1.29829900
C -17.82750900 3.45290100 1.45289800
H -16.21433700 2.06802900 1.81210800
C -18.97758100 3.72831400 0.70877900
H -20.27631900 3.03116700 -0.86629100
H -17.50167200 4.14099500 2.22712700
H -19.54688200 4.63336700 0.89470500
C -17.45034600 -1.02096300 -0.23469800
C -18.57418400 -1.34966100 0.53799300
C -17.01648700 -1.91050100 -1.22914700
C -19.25408500 -2.54472100 0.31118400

H -18.90850800 -0.66521600 1.30986400
C -17.69130600 -3.11200100 -1.43598600
H -16.15272500 -1.65479100 -1.83293500
C -18.81561600 -3.43531000 -0.67204400
H -20.12276900 -2.78591200 0.91641300
H -17.34412200 -3.79103900 -2.20893900
H -19.34333300 -4.36842300 -0.84113600
N -11.12902400 0.40656300 -0.10323500
C -10.39619100 -0.64579300 -0.19518000
H -10.82629400 -1.64966900 -0.30641400
C -8.93577600 -0.58239500 -0.17709200
C -8.25135100 0.64049900 -0.03861300
C -8.19214300 -1.76858300 -0.30001300
C -6.86771900 0.67572300 -0.02492700
H -8.83010400 1.55239200 0.05598800
C -6.80408300 -1.74316200 -0.28535100
H -8.71277300 -2.71595000 -0.40647500
C -6.11962500 -0.51842400 -0.14697600
H -6.34223700 1.61870000 0.08137800
H -6.23609200 -2.66218400 -0.37958000
C -4.70165400 -0.47851000 -0.12792800
C -3.48545100 -0.42975100 -0.10798400
C -2.07104400 -0.38327700 -0.08383500
C -1.40394800 0.86184300 0.07174600
C -1.32208500 -1.56732800 -0.21220700
C -0.01563800 0.89205000 0.09563600
C 0.07000300 -1.53940700 -0.18841700
H -1.85875400 -2.49883500 -0.32944600
C 0.73449700 -0.29576400 -0.03231300
H 0.52172000 1.82324800 0.21307600
C 2.14469300 -0.24617400 -0.00384100
C 3.36081800 -0.19148000 0.02310400
C 4.76947000 -0.13736200 0.05543800
C 5.43537700 1.10178200 0.19615500
C 5.53180800 -1.32275700 -0.05752400
C 6.82226400 1.11522400 0.23167600
H 4.86288200 2.01631000 0.27302300
C 6.91634700 -1.23539500 -0.01864000
H 5.03137000 -2.27421300 -0.17866400
C 7.89476500 -2.32540000 -0.15372700
C 7.56856800 -3.66726500 -0.31690700
C 8.59508300 -4.59850700 -0.46847500
H 6.53173200 -3.97854200 -0.32797200
C 10.17452800 -2.80176700 -0.28912000
C 9.91593600 -4.15990700 -0.46086500
H 8.36181200 -5.64932100 -0.59612200
H 11.18634400 -2.42210000 -0.28731400

H 10.74263200 -4.84817300 -0.58603700
C 7.71609000 2.27384400 0.38019200
C 7.30142300 3.58679400 0.56698900
C 9.96706400 2.89790700 0.51583000
C 8.26715100 4.58032200 0.73154500
H 6.24625100 3.82839400 0.59111900
C 9.61414700 4.23161400 0.71324800
H 10.99688900 2.58080000 0.46788000
H 7.96528900 5.61104200 0.87869300
H 10.39196700 4.97322000 0.84695200
N 7.50470600 -0.03900900 0.14091200
N 9.03999800 1.94910000 0.34483400
N 9.19131600 -1.91088800 -0.12828400
Co 9.36361900 0.04208200 0.08691000
C 11.83590800 -0.40872200 1.33943000
C 13.14963600 -0.83900400 1.51097800
C 14.01610800 -0.80521200 0.42414700
C 13.55778900 -0.29046500 -0.78157300
C 12.23559900 0.15405400 -0.89726900
H 13.48428700 -1.21557100 2.46791300
H 15.03751600 -1.15381300 0.52402100
H 14.21788400 -0.19499900 -1.63447400
N 11.37409800 0.04314800 0.14015000
C 11.84422100 0.83973700 -2.15883600
C 12.09853300 0.24745800 -3.39905800
C 11.08107800 2.76970300 -3.14147200
C 11.79454100 0.96837100 -4.55170200
H 12.49994200 -0.75796900 -3.45594800
C 11.27282400 2.25519900 -4.42485600
H 10.68804600 3.77336500 -2.99901700
H 11.96196500 0.53186000 -5.53068900
H 11.02499100 2.85163500 -5.29557800
C 10.84665400 -0.43168000 2.42967000
C 11.16545900 -0.65058000 3.77015600
C 10.14881800 -0.62559000 4.72084300
H 12.18966700 -0.82295400 4.07219200
C 8.59196100 -0.16928600 2.96001900
C 8.84014200 -0.38007100 4.31153600
H 10.37972600 -0.79035100 5.76708200
H 7.59042300 0.02373100 2.60121500
H 8.02004800 -0.34797400 5.01809200
N 11.35914600 2.08455200 -2.02578800
N 9.57214600 -0.19537500 2.04716900
O -2.20340600 1.95258200 0.18834300
O 0.86472300 -2.63022000 -0.30488700
C -1.57776500 3.22461500 0.34798600
H -0.94567300 3.46676400 -0.51363800

H -2.38901600 3.94854400 0.41906900
H -0.97588300 3.25851400 1.26299600
C 0.23962400 -3.90400000 -0.46603000
H -0.39186700 -4.14635100 0.39543300
H -0.36082500 -3.93660000 -1.38149500
H 1.05246400 -4.62594500 -0.53707800
O 9.21763200 0.12644900 -1.74826700
H 9.29117700 1.06176100 -1.97795800

O* (TPA-tpd-Co-O)

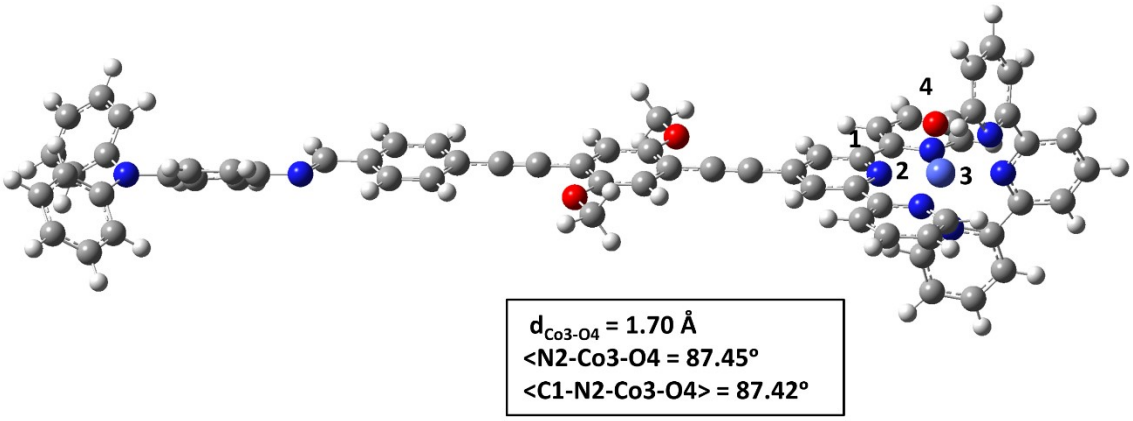


Fig S32. Optimized structure of **TPA-tpd-Co-O** obtained from DFT computation at B3LYP/6-31G** level (LANL2DZ: basis set and electron core potential of Co; solvent = water)

XYZ coordinates

Charge 2, multiplicity 2

N -16.74124600 0.18867100 0.00933800
C -15.33070700 0.22579000 -0.00460300
C -14.58178800 -0.87070300 0.45887500
C -14.64593800 1.36450500 -0.46288700
C -13.19442300 -0.84223300 0.43640200
H -15.09837200 -1.74100400 0.84772700
C -13.25854000 1.40173300 -0.45156800
H -15.20905800 2.22005000 -0.81787400
C -12.50349500 0.29275500 -0.03160500
H -12.64129700 -1.68817000 0.83161000
H -12.73099000 2.28345000 -0.80081500
C -17.48500900 1.35693200 0.32114700
C -18.63488300 1.67906200 -0.41476900
C -17.08245100 2.19687300 1.37007400

C -19.37125000 2.81913500 -0.09862600
H -18.94481600 1.03230200 -1.22826000
C -17.81425600 3.34503400 1.66691200
H -16.19803900 1.94510700 1.94501400
C -18.96421500 3.66149800 0.93911500
H -20.25965600 3.05625800 -0.67618200
H -17.49101600 3.98655300 2.48117700
H -19.53596200 4.55248600 1.17794400
C -17.42655200 -1.01969800 -0.28084300
C -18.54694200 -1.39592400 0.47490200
C -16.99483000 -1.84741000 -1.32815600
C -19.22568400 -2.57663100 0.17976400
H -18.87932500 -0.75927500 1.28744300
C -17.66841600 -3.03573500 -1.60382600
H -16.13375100 -1.55446500 -1.91875000
C -18.78930000 -3.40614500 -0.85638800
H -20.09167800 -2.85517500 0.77267800
H -17.32306300 -3.66685000 -2.41715300
H -19.31606400 -4.32853200 -1.07888200
N -11.10718900 0.40857700 -0.06580800
C -10.37187800 -0.63482600 -0.21950800
H -10.79948000 -1.63144300 -0.38969400
C -8.91167300 -0.56906100 -0.19751200
C -8.23025200 0.64560800 0.01071000
C -8.16515600 -1.74449300 -0.38788900
C -6.84671000 0.68347100 0.02603700
H -8.81137600 1.54905400 0.15749700
C -6.77717800 -1.71655200 -0.37153600
H -8.68345900 -2.68551000 -0.54843200
C -6.09569700 -0.49993400 -0.16389600
H -6.32352500 1.62016800 0.18577600
H -6.20691400 -2.62730200 -0.51793100
C -4.67783300 -0.45775700 -0.14352100
C -3.46168300 -0.40778000 -0.12240600
C -2.04736600 -0.36031700 -0.09804500
C -1.38158900 0.87936700 0.10060500
C -1.29713500 -1.53813400 -0.26926300
C 0.00674500 0.91067500 0.12267100
C 0.09490600 -1.50924100 -0.24623600
H -1.83281000 -2.46563500 -0.41843500
C 0.75820000 -0.27086800 -0.04803100
H 0.54308600 1.83797300 0.27144400
C 2.16842500 -0.22127900 -0.02071900
C 3.38471500 -0.16891800 0.00480800
C 4.79383600 -0.12099900 0.03333300
C 5.47117100 1.10363500 0.20083700
C 5.55373500 -1.30152300 -0.09258800

C 6.85976900 1.11551500 0.22038600
H 4.90201000 2.01470700 0.32183700
C 6.94063300 -1.22667900 -0.06149700
H 5.04560100 -2.24888400 -0.20517100
C 7.83693200 -2.40561800 -0.15305000
C 7.37462600 -3.71435800 -0.30276200
C 8.30212700 -4.75282900 -0.36679700
H 6.31575300 -3.92755700 -0.36867900
C 10.04861900 -3.13287500 -0.13404300
C 9.66231600 -4.46353600 -0.28165300
H 7.96192500 -5.77570300 -0.48300600
H 11.09428000 -2.85231700 -0.06855500
H 10.41231500 -5.24369700 -0.32990600
C 7.67950800 2.33400800 0.42736900
C 7.14830800 3.62000800 0.52880300
C 9.84585200 3.14023000 0.72857900
C 8.01834600 4.68882200 0.74190600
H 6.08364700 3.79258500 0.43940700
C 9.38712200 4.45086500 0.84840900
H 10.89888500 2.89339100 0.77206900
H 7.62624600 5.69656700 0.82182800
H 10.09026600 5.25800800 1.01467100
N 7.55412000 -0.03436000 0.08571700
N 9.00778500 2.12200000 0.52681100
N 9.15698000 -2.14215000 -0.06934200
Co 9.54299200 0.06093900 0.02613400
C 12.07447500 -0.47560600 1.18959700
C 13.41307100 -0.85461500 1.26647000
C 14.22222300 -0.69935500 0.14436600
C 13.69062400 -0.12697800 -1.00690500
C 12.34835900 0.25774300 -1.02384400
H 13.81416800 -1.27571100 2.17862600
H 15.26245000 -1.00224800 0.17698700
H 14.30462800 0.05337300 -1.88050000
N 11.55584000 0.03984000 0.04444300
C 11.78031100 0.99249800 -2.18412800
C 11.85653600 0.47526000 -3.48234500
C 10.77679800 2.92378900 -2.90702600
C 11.33963000 1.24017700 -4.52571700
H 12.28768900 -0.50374000 -3.65832200
C 10.78668000 2.48654200 -4.23516500
H 10.36200800 3.89424000 -2.64618400
H 11.36685900 0.86874900 -5.54441900
H 10.37672200 3.11466300 -5.01809000
C 11.11948700 -0.59036800 2.30344500
C 11.46481700 -0.95244100 3.60423900
C 10.47169400 -0.99813100 4.57984100

H 12.49074800 -1.18587500 3.85647700
C 8.88000600 -0.32945200 2.91989100
C 9.15954500 -0.67827600 4.23626200
H 10.72366500 -1.27614900 5.59688400
H 7.87641900 -0.07867000 2.60333900
H 8.36083100 -0.69633400 4.96730900
N 11.26546500 2.20302700 -1.89625400
N 9.83695500 -0.29007700 1.98311100
O -2.18232300 1.96412900 0.25735300
O 0.89075700 -2.59432700 -0.40198800
C -1.55803300 3.23065200 0.46047100
H -0.92837200 3.50401100 -0.39355500
H -2.37010800 3.95042300 0.55904700
H -0.95397300 3.23306800 1.37467800
C 0.26693100 -3.86259700 -0.60588700
H -0.36274000 -4.13528100 0.24780600
H -0.33510800 -3.86448100 -1.52090300
H 1.08054400 -4.58060700 -0.70318100
O 9.40921200 0.22089000 -1.66212200

HOO* (TPA-tpd-Co-OOH)

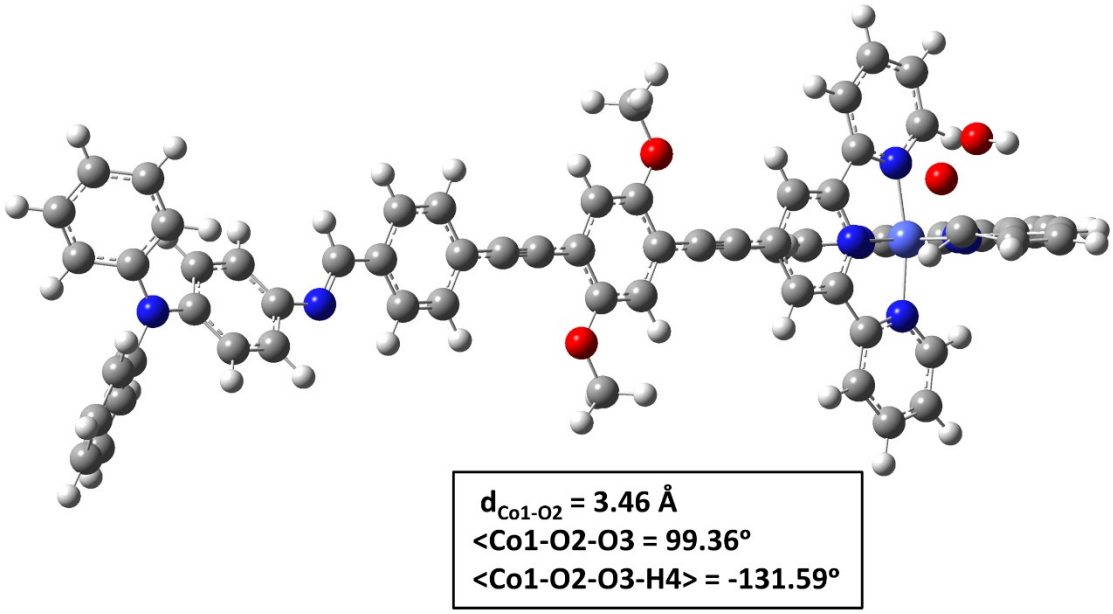


Fig S33. Optimized structure of **TPA-tpd-Co-OOH** obtained from DFT computation at B3LYP/6-31G** level (LANL2DZ: basis set and electron core potential of Co; solvent = water)

XYZ coordinates

Charge 2, multiplicity 1

N -16.75942500 0.17958200 0.00003700
C -15.34907900 0.21479300 -0.02670100
C -14.59655900 -0.70060400 0.73079500
C -14.66801500 1.17539100 -0.79416200
C -13.20933400 -0.67680300 0.69822800
H -15.11029100 -1.42350000 1.35449300
C -13.28068900 1.21711800 -0.79704900
H -15.23388900 1.89174100 -1.37869400
C -12.52206500 0.27715600 -0.07787500
H -12.65367600 -1.37220900 1.31899200
H -12.75584600 1.96242600 -1.38590600
C -17.50683700 1.38586000 -0.03744100
C -18.65770700 1.47867900 -0.83395600
C -17.10693100 2.49379000 0.72441900
C -19.39757100 2.65930100 -0.85948600
H -18.96553800 0.62391000 -1.42618400
C -17.84227700 3.67659800 0.67808000
H -16.22176900 2.42108700 1.34677800
C -18.99313300 3.76636800 -0.10915900
H -20.28664600 2.71714500 -1.48017500
H -17.52111500 4.52667000 1.27247200
H -19.56755200 4.68672300 -0.13698100
C -17.44116500 -1.06320900 0.06964200
C -18.55872400 -1.21036200 0.90469200
C -17.00872300 -2.15474100 -0.69837200
C -19.23393100 -2.42800200 0.96184700
H -18.89160500 -0.36860400 1.50192100
C -17.67884700 -3.37405700 -0.62060100
H -16.14988500 -2.04050800 -1.35061800
C -18.79680900 -3.51809900 0.20502000
H -20.09770800 -2.52763500 1.61225500
H -17.33309200 -4.21057700 -1.22040200
H -19.32084000 -4.46701300 0.25731500
N -11.12621000 0.38162000 -0.14734100
C -10.38714700 -0.65906800 0.00676000
H -10.81078000 -1.66372200 0.13419600
C -8.92711400 -0.58479300 0.00540800
C -8.25002400 0.63956000 -0.15475700
C -8.17631900 -1.76167700 0.16812600
C -6.86663400 0.68476300 -0.15446400
H -8.83420700 1.54434600 -0.27935000
C -6.78842400 -1.72556900 0.17289500
H -8.69118700 -2.70998800 0.29277500
C -6.11137000 -0.49956500 0.01127300
H -6.34680900 1.62862200 -0.27915900

H -6.21489600 -2.63713600 0.30018900
C -4.69368400 -0.44808100 0.01514300
C -3.47779400 -0.38842700 0.01743700
C -2.06385300 -0.32743100 0.02363900
C -1.40625000 0.91705300 -0.17353700
C -1.30612300 -1.49538800 0.22597100
C -0.01838100 0.96275500 -0.16249300
C 0.08575500 -1.45195000 0.23789400
H -1.83577300 -2.42671800 0.37265100
C 0.74074600 -0.20877800 0.04174300
H 0.51199000 1.89383400 -0.30891900
C 2.15007600 -0.14284100 0.05207000
C 3.36590000 -0.07344600 0.06022900
C 4.77328100 -0.00031500 0.07280100
C 5.42671700 1.23831800 -0.12908200
C 5.54594000 -1.16461400 0.29129900
C 6.81264800 1.27201400 -0.10808600
H 4.84390400 2.13462500 -0.29308300
C 6.92872200 -1.05889600 0.29571400
H 5.05326800 -2.11430200 0.45062000
C 7.92141500 -2.12428500 0.49835400
C 7.61947500 -3.46357700 0.70957600
C 8.66341300 -4.37451300 0.86620000
H 6.58783100 -3.79045300 0.74405600
C 10.21247500 -2.56399800 0.59453600
C 9.97733900 -3.92008800 0.80622900
H 8.44867700 -5.42439500 1.02946000
H 11.21797500 -2.17051700 0.53844300
H 10.81668700 -4.59512800 0.91826300
C 7.69818000 2.43393100 -0.28848400
C 7.27176200 3.73295000 -0.54239800
C 9.93945500 3.09774000 -0.34353600
C 8.22499800 4.73853000 -0.69789500
H 6.21459700 3.95428200 -0.61899800
C 9.57635000 4.41779100 -0.59805900
H 10.97733600 2.80380300 -0.26297100
H 7.91239700 5.75729800 -0.89604300
H 10.34715500 5.16941000 -0.71492500
N 7.50797300 0.13854200 0.09923900
N 9.02433100 2.13522100 -0.18984100
N 9.21140100 -1.69076700 0.45277000
Co 9.37199700 0.23443700 0.13495500
C 11.83151200 0.53798400 1.39343500
C 13.21816300 0.58829100 1.46605200
C 13.94822400 0.39953700 0.28409100
C 13.30555200 0.17034400 -0.92857100
C 11.90570800 0.12889600 -0.95154800

H 13.72394300 0.76525300 2.40629100
H 15.03118000 0.43285700 0.31752200
H 13.87424600 0.02521000 -1.83780700
N 11.23763600 0.31617500 0.20282400
C 11.00550300 -0.08220000 -2.08390100
C 11.44372500 -0.24157000 -3.37708500
C 8.67064200 -0.38151600 -2.67556900
C 10.45392900 -0.28850600 -4.40501700
H 12.49973800 -0.25987100 -3.61071700
C 9.13257800 -0.26928200 -4.09137500
H 7.74670500 0.18161900 -2.50050500
H 10.76781900 -0.28818300 -5.44489100
H 8.36534200 -0.24019400 -4.85774000
C 10.85667000 0.69114900 2.48395800
C 11.18320900 0.93546400 3.81439700
C 10.15772600 1.05766700 4.75034900
H 12.21987300 1.02830000 4.11251600
C 8.57454000 0.68782300 2.98773100
C 8.83449500 0.93277000 4.33308600
H 10.39238500 1.24758900 5.79146500
H 7.56176900 0.58271800 2.62077200
H 8.00988600 1.02120000 5.02948200
N 9.67828500 -0.02053600 -1.73991700
N 9.55840900 0.56961900 2.08862100
O -2.21417900 1.99127700 -0.36205900
O 0.88865800 -2.52621700 0.42665600
C -1.59844900 3.26212500 -0.56450000
H -0.97171800 3.26059200 -1.46332000
H -2.41540500 3.97178900 -0.69176900
H -0.99337600 3.55216000 0.30173900
C 0.27366900 -3.79938000 0.62779800
H -0.35257900 -3.79833800 1.52641200
H -0.32970900 -4.08821000 -0.23944200
H 1.09239600 -4.50687700 0.75455300
O 8.12814200 -1.74119800 -2.42844900
O 9.20796300 -2.70229200 -2.53048800
H 9.37019400 -2.71092700 -3.49141600

HER reaction intermediate

H* (TPA-tpd-Co-H)

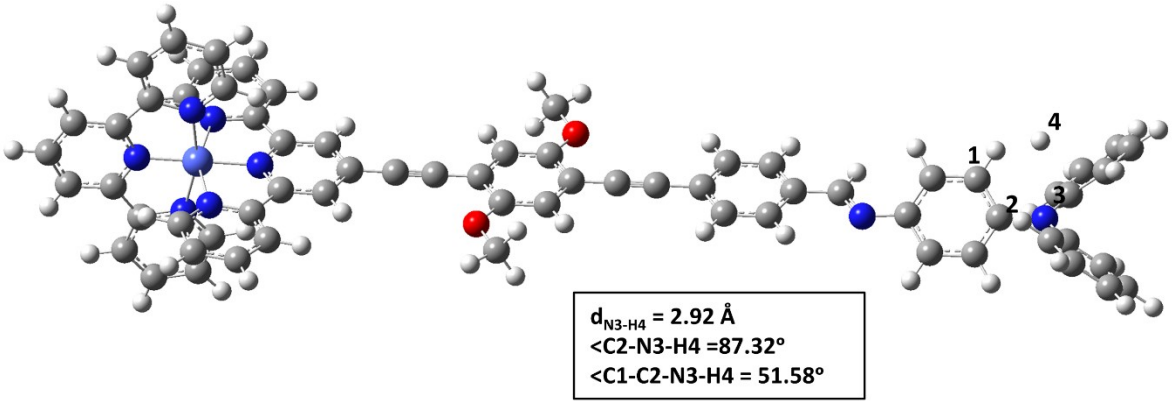


Fig S34. Optimized structure of **TPA-tpd-Co-OOH** obtained from DFT computation at B3LYP/6-31G** level (LANL2DZ: basis set and electron core potential of Co; solvent = water)

XYZ coordinates

Charge 2, multiplicity 1
N 16.48074900 0.23307100 -0.00097300
C 15.07070900 0.26646800 0.04091200
C 14.30963000 -0.68752200 -0.65820400
C 14.39818900 1.26605000 0.76488700
C 12.92255800 -0.66050000 -0.61150400
H 14.81565400 -1.44416800 -1.24682200
C 13.01107200 1.30992200 0.78021400
H 14.97074800 2.01184100 1.30439800
C 12.24434600 0.33410200 0.11955500
H 12.35924300 -1.38745000 -1.18763700
H 12.49328800 2.08611100 1.33441900
C 17.22456900 1.44067600 -0.05733600
C 18.40350900 1.57618200 0.69044800
C 16.79625500 2.50534800 -0.86422900
C 19.14352300 2.75495500 0.62291300
H 18.73326000 0.75482000 1.31720600
C 17.53277500 3.68756000 -0.91112400
H 15.88837300 2.40037800 -1.44773700
C 18.71165400 3.81913100 -0.17302100
H 20.05468900 2.84578300 1.20649900
H 17.18948000 4.50376200 -1.53964000
H 19.28639200 4.73863600 -0.21754800
C 17.16350000 -1.01004800 -0.05059700
C 18.25345900 -1.18568800 -0.91627600
C 16.75676300 -2.07505200 0.76689800
C 18.92590700 -2.40574300 -0.95586500
H 18.56792000 -0.36410900 -1.55014100

C 17.42352900 -3.29717000 0.70712900
H 15.91920600 -1.93852100 1.44218200
C 18.51355500 -3.46981300 -0.14997000
H 19.76796000 -2.52757900 -1.63051700
H 17.09748500 -4.11314000 1.34504400
H 19.03523400 -4.42068200 -0.18838700
N 10.84908300 0.44270500 0.19565300
C 10.11146200 -0.60761400 0.12002400
H 10.53784600 -1.61746700 0.05943100
C 8.65123900 -0.53779500 0.12759300
C 7.97043000 0.69312000 0.19257400
C 7.90368400 -1.72643500 0.06763800
C 6.58669200 0.73382700 0.19909200
H 8.55167700 1.60720700 0.23791900
C 6.51579500 -1.69523100 0.07222500
H 8.42117400 -2.68011400 0.01644400
C 5.83476100 -0.46224900 0.13773800
H 6.06517600 1.68363800 0.24949500
H 5.94418900 -2.61564600 0.02508900
C 4.41648400 -0.42362700 0.14017000
C 3.19941700 -0.39781300 0.14029000
C 1.78433100 -0.35423100 0.13828100
C 1.03478000 -1.56005500 0.10027000
C 1.11578100 0.88356200 0.17189500
C -0.35343700 -1.49947500 0.09490900
C -0.27516700 0.94610400 0.16661700
H 1.71403200 1.78403400 0.20047800
C -1.02235900 -0.25872900 0.12683400
H -0.95220500 -2.39967600 0.06542700
C -2.43461700 -0.21481700 0.11575400
C -3.65130000 -0.18375800 0.10258400
C -5.06280200 -0.12834600 0.08120100
C -5.83340300 -1.30553900 0.03582200
C -5.73041600 1.11122000 0.10068400
C -7.22028400 -1.21343200 0.00878000
H -5.33632600 -2.26543100 0.01941400
C -7.11966400 1.13950700 0.07228800
H -5.15198100 2.02392900 0.13457100
C -7.92241000 2.38615000 0.08575900
C -7.36320600 3.66457400 0.14379800
C -8.21284800 4.76942100 0.15178400
H -6.29062500 3.80442300 0.18292000
C -10.07084400 3.26400200 0.04618300
C -9.59137600 4.57179300 0.10225200
H -7.79925700 5.77081900 0.19653800
H -11.13493900 3.05321100 0.00659800
H -10.28304100 5.40589400 0.10686800

C -8.12664200 -2.38591400 -0.04455300
C -7.67767800 -3.70838700 -0.05234000
C -10.34075700 -3.07533200 -0.13858900
C -8.61713900 -4.73645100 -0.10668600
H -6.62097000 -3.94022900 -0.01655800
C -9.97346500 -4.42013600 -0.15136300
H -11.38342600 -2.77521800 -0.17122100
H -8.29005300 -5.77032500 -0.11374300
H -10.73322700 -5.19154800 -0.19458000
N -7.83492600 -0.00829900 0.02608900
N -9.44285300 -2.08879400 -0.08630000
N -9.25905600 2.20437700 0.03823900
Co -9.76578200 0.07796600 -0.04005300
C -12.33617600 0.17869200 1.04483900
C -13.72855200 0.26009700 1.02250300
C -14.37146500 0.33479600 -0.21352000
C -13.63374400 0.32904700 -1.39779300
C -12.24345500 0.24752400 -1.31533800
H -14.29973000 0.26660900 1.94182900
H -15.45275400 0.39846600 -0.25401100
H -14.13169800 0.38736900 -2.35714400
N -11.64417600 0.17468900 -0.11097900
C -11.28358500 0.22975900 -2.43342000
C -11.63709900 0.29069300 -3.77892800
C -9.02011500 0.12008000 -2.97117700
C -10.62985100 0.26356000 -4.74255700
H -12.67762900 0.35772500 -4.07060800
C -9.30093900 0.17658900 -4.33481000
H -8.00187400 0.05209800 -2.60792400
H -10.88325000 0.30957000 -5.79569300
H -8.48965300 0.15251100 -5.05225100
C -11.46705900 0.09311300 2.23190300
C -11.92590000 0.07099700 3.54652900
C -10.99740200 -0.01292000 4.58322600
H -12.98686800 0.11693400 3.75846200
C -9.25225000 -0.04575000 2.93871900
C -9.63994000 -0.07200600 4.27688300
H -11.33302600 -0.03180100 5.61395800
H -8.20799800 -0.08916300 2.65373300
H -8.88724200 -0.13754700 5.05319200
N -9.98298100 0.14626400 -2.04331600
N -10.13934900 0.03417300 1.94102000
O 1.75844800 -2.70862600 0.07083200
O -0.99509300 2.09450100 0.19607600
C 1.04783800 -3.94464600 0.02881300
H 0.42877600 -4.01618000 -0.87250400
H 1.80830500 -4.72484000 0.01046400

H 0.41669600 -4.07008000 0.91571100
C -0.28475000 3.33204300 0.23828400
H 0.33351800 3.40309100 1.13975300
H 0.34554700 3.45729100 -0.64880700
H -1.04659800 4.11074900 0.25672700
H 16.25573900 0.14400900 -2.91215000

References

[1] K. Wariishi, S. I. Morishima and Y. Inagaki, A Facile Synthesis of 1,4-Dialkoxy-2,5-diiodobenzenes: Reaction of Dialkoxybenzenes with Iodine Monochloride in Alcoholic Solvents Org. Process Res. Dev., 2003, 7, 98.

[2] W. Fu, L. Dong, J. Shi, B. Tong, Z. Cai, J. Zhi and Y. Dong, Synthesis of Polyquinolines via One-Pot Polymerization of Alkyne, Aldehyde, and Aniline under Metal-Free Catalysis and Their Properties, Macromolecules, 2018, 51, 3254.

[3] V. Grosshenny, F. M. Romero and R. Ziessel, Construction of Preorganized Polytopic Ligands via Palladium-Promoted Cross-Coupling Reactions, J. Org. Chem. 1997, 62, 5, 1491.

[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, Gaussian 09 (Revision C.01); Gaussian Inc.: Wallingford, CT. 2009.

[5] K. Kim, K. D. Jordan, Comparison of Density Functional and MP2 Calculations on the Water Monomer and Dimer. J. Phys. Chem. 1994, 98, 10089.

[6] P. J . Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. J. Phys. Chem. 1994, 98, 11623.

[7] A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior. Phys. Rev. A 1988, 38, 3098.

[8] C. Lee, W. Yang, R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B 1988, 37, 785.

[9] S. H. Vosko, L. Wilk, M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can. J. Phys. 1980, 58, 1200.

[10] A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98, 5648.

[11] P. J. Hay, W. R. Wadt, Ab initio effective core potentials for molecular calculations.

Potentials for the transition metal atoms Sc to Hg. J. Chem. Phys. 1985, 82, 270.

[12] W. R. Wadt, P. J. Hay, Ab initio effective core potentials for molecular calculations.

Potentials for main group elements Na to Bi. J. Chem. Phys. 1985, 82, 284.

[13] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Ding, F. Williams, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman,D. J. Fox, Wallingford, CT, 2016

[14] A´. Valde´s, Z.-W. Qu, G.-J. Kroes, J. Rossmeisl, J. K. Nørskov, Oxidation and Photo-Oxidation of Water on TiO2 Surface, J. Phys. Chem. C 2008, 112, 9872–9879.

[15] Y. Jia, L. Zhang, A. Du, G. Gao, J Chen, X. Yan, C. L. Brown, X. Yao, Defect Graphene as a Trifunctional Catalyst for Electrochemical Reactions, Adv. Mater. 2016, 28, 9532–9538.

[16] P. Wang, X. Zhang, J. Zhang, S. Wan, S. Guo, G. Lu, J. Yao, X. Huang, Precise tuning in platinum-nickel/nickel sulfide interface nanowires for synergistic hydrogen

evolution catalysis, Nat. Commun, 2017, 8, 14580.

[17] J. K. Norskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov, U. Stimming, Trends in the exchange current for hydrogen evolution. J. Electrochem. Soc. 2003, 152, J23–J26.

[18] Y. Jia, L. Zhang, A. Du, G. Gao, J. Chen, X. Yan, C. L. Brown, X. Ya, Defect Graphene as a Trifunctional Catalyst for Electrochemical Reactions, Adv.Mater.2016, 28, 9532.

[19] R. Jiang, D. R. Baker, D. T. Tran, J. Li, A. C. Leff, and S. S. Zhang, Multimetallic $FeCoNiO_x$ Nanoparticles Covered with Nitrogen-Doped Graphene Layers as Trifunctional Catalysts for Hydrogen Evolution and Oxygen Reduction and Evolution, ACS Appl. Nano Mater. 2020, 3, 7, 7119.

[20] B. Devi, R. R. Koner, and A. Halder, Ni(II)-Dimeric Complex-Derived Nitrogen-Doped Graphitized Carbon-Encapsulated Nickel Nanoparticles: Efficient Trifunctional Electrocatalyst for Oxygen Reduction Reaction, Oxygen Evolution Reaction, and Hydrogen Evolution Reaction, ACS Sustainable Chem. Eng. 2019, 7, 2, 2187.

[21] X. Fan, F. Kong, A. Kong, A. Chen, Z. Zhou, and Y. Shan, Covalent Porphyrin Framework-Derived Fe_2P@Fe_4N-Coupled Nanoparticles Embedded in N-Doped Carbons as Efficient Trifunctional Electrocatalysts, ACS Appl. Mater. Interfaces 2017, 9, 38, 32840.

[22] X. Chen, B. Shao, M. Tang, X. He, F. Yang, Z. Guo, Z. Zhang, C. He, F. Huang and J. Huang, Accurately metal-modulated bimetallic metal– organic frameworks as advanced trifunctional electrocatalysts, J. Mater. Chem. A, 2021, 9, 14682.

[23] S. Chen, F. Bi, K. Xiang, Y. Zhang, P. Hao, M. Li, B. Zhao and X. Guo**,** Reactive Template-Derived CoFe/N-Doped Carbon Nanosheets as Highly Efficient Electrocatalysts toward Oxygen Reduction, Oxygen Evolution, and Hydrogen Evolution, ACS Sustainable Chem. Eng. 2019, 7, 18, 15278.

[24] L. Zhang, Y. Zhu, Z. Nie, Z. Li, Y. Ye, L. Li, J. Hong, Z. Bi, Y. Zhou and G. Hu**,** Co/MoC Nanoparticles Embedded in Carbon Nanoboxes as Robust Trifunctional Electrocatalysts for a Zn–Air Battery and Water Electrocatalysis, ACS Nano, 2021, 15, 8, 13399.

[25] C. Hu, L. Dai, Multifunctional Carbon-Based Metal-Free Electrocatalysts for Simultaneous Oxygen Reduction, Oxygen Evolution, and Hydrogen Evolution, Adv. Mater., 2017, 29, 1604942.

[26] Z. Diao, Y. Qiu, S. Liu, W. Wang, K. Chen, H. Li, W. Yuan, Y. Qu, X. Guo, Interfacial Engineering of W_2N/WC Heterostructures Derived from Solid-State Synthesis: A Highly Efficient Trifunctional Electrocatalyst for ORR, OER, and HER, Adv. Mater., 2019, 32, 1905679.

[27] Z. Yang, C. Zhao, Y. Qu, H. Zhou, F. Zhou, J. Wang, Y. Wu, Y. Li, Trifunctional Self-Supporting Cobalt-Embedded Carbon Nanotube Films for ORR, OER, and HER Triggered by Solid Diffusion from Bulk Metal, Adv. Mater., 2019, 31, 1808043.

[28] X. Wang, X. Zhou, C. Li, H. Yao, C. Zhang, J. Zhou, R. Xu, L. Chu, H. Wang, M. Gu, H. Jiang, M. Huang, Asymmetric CoN3P1 Trifunctional Catalyst with Tailored Electronic Structures Enabling Boosted Activities and Corrosion Resistance in an Uninterrupted Seawater Splitting System, Adv.Mater., 2022, 2204021.