

Article

Electrochemical Stimuli Driven Facile Metal Free Hydrogen Evolution from Pyrene-Porphyrin Based Crystalline Covalent Organic Framework.

Subhajit Bhunia, Sabuj Kanti Das, Rajkumar Jana, Sebastian C. Peter, Santanu Bhattacharya, Matthew Addicoat, Asim Bhaumik, and Anirban Pradhan

ACS Appl. Mater. Interfaces, **Just Accepted Manuscript** • DOI: 10.1021/acsami.7b06968 • Publication Date (Web): 26 Jun 2017Downloaded from <http://pubs.acs.org> on June 26, 2017**Just Accepted**

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

Electrochemical Stimuli Driven Facile Metal Free Hydrogen Evolution from Pyrene-Porphyrin Based Crystalline Covalent Organic Framework.

Subhajit Bhunia,^{†,||} Sabuj Kanti Das,^{‡,||} Rajkumar Jana,[§] Sebastian C Peter,[§] Santanu Bhattacharya,^{,†} Matthew Addicoat,^{*,¥} Asim Bhaumik,^{*,‡} and Anirban Pradhan^{*,†}*

[†]Director's Research Unit, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, India.

[‡]Department of Material Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata- 700032, India.

[§]New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore- 560064, India

[¥]School of Science and Technology, Nottingham Trent University, Nottingham, NG11 8NS, UK.

ABSTRACT:

A [2+2] Schiff base type condensation between 5, 10, 15, 20-tetrakis(4-aminophenyl)porphyrin (TAP) and 1,3,6,8-tetrakis (4-formylphenyl) pyrene (TFFPy) under solvothermal condition yields a crystalline, quasi-two dimensional covalent organic framework (SB-PORPy-COF). The porphyrin and pyrene units are alternatively occupied in the vertex of 3D triclinic crystal having permanent micro-porosity with moderately high surface area ($\sim 869 \text{ m}^2\text{g}^{-1}$) and promising chemical stability. The AA stacking of the monolayers give a pyrene bridged conducting channel. SB-PORPy-COF has been exploited for metal free hydrogen production to understand the electrochemical behavior using the imine based docking site in acidic media. SB-PORPy-COF has shown the onset potential of 50 mV and the Tafel slope of 116 mV dec^{-1} . We expect that the addendum of the imine based COF would not only enrich the structural variety but also help to understand the electrochemical behavior of these class of materials.

KEYWORDS: Covalent organic framework, Porosity, Hydrogen evolution reaction, Electrochemical, Metal free, Porphyrin based.

1. INTRODUCTION

Covalent organic frameworks (COFs)¹⁻⁶ constructed from organic building blocks via covalent bonds are a unique kind of crystalline porous material with structural periodicity and inherent porosity of uniform topology. Besides them, recently some unique strategy has been developed to obtain morphologically tunable crystalline highly porous carbon materials by controlled thermal annealing of crystalline MOFs.⁷⁻⁹ Due to the atomically precise pore apertures, resulting from strong and rigid covalent linkages between light elements (H, B, C, N and O) through the thermodynamically controlled reversible bond formation, COFs often show excellent and unique properties such as gas storage and separation,¹⁰⁻¹⁴ molecular catalysis,¹⁵⁻¹⁹ drug delivery²⁰⁻²² etc.

1
2
3 The two-dimensional COFs are more promising than the three-dimensional COFs because of two
4 factors. The first factor is due to the inherent stacking between the two adjacent layers (π - π
5 interaction). Because of the stacking phenomena, 2D COFs expedite the charge carrier
6 mobility²²⁻²⁴ through the multi-stacked columnar channel which results in promising
7 optoelectronic phenomena, conductivity²⁵⁻²⁸ and electroactivity²⁹⁻³² etc. The connectivity of the
8 selected organic building blocks plays an important role on COFs' geometry^{33, 34} which may lead
9 to the formation of two dimensional (2D) or three dimensional (3D) crystalline networks having
10 different pore apertures. Selecting and comprising some electro-active molecular unit such as
11 porphyrin^{35, 36}, phthalocyanine, pyrene,³⁷ tetrathiafulvalene and thiophene^{38, 39} derivatives, the
12 stacking pattern may be tuned to different extent such as AA (eclipsed), AB (staggered), serrated
13 and inclined arrangements which results in the different extent of electronic coupling between
14 two layers. The second factor is the degree of lateral conjugation from π orbitals present
15 throughout the individual 2D layer. The molecular assembly of alternating donor acceptor
16 moiety boosts the charge carrier mobility over the single layer. Electrochemical hydrogen
17 production^{40, 41} from water holds an exceptional promise towards sustainable source of carbon
18 free high purity energy at low cost price. The development of productive electrocatalyst mainly
19 consists of two factors, (1) the reaction kinetics of hydrogen production and (2) the overpotential
20 value. Noble metal containing systems hold maximum hydrogen evolution reaction (HER)
21 properties with low overpotential (η) than any other metal based system.^{42, 43} In the past decades
22 many attempts have been made to develop noble metal free system containing electrochemically
23 responsive transition metals based Co, Fe, Ni, Mo-complexes. But often metal ions leaches away
24 from making the electrocatalytic system toxic. The new challenge requires the invention of metal
25 free electro-catalyst to overcome the environmental hazard and facilitate the greener way of
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 production of clean and high purity energy. The π -electronic conjugation, low band gap and
4 active side-groups etc. make an organic system electrochemically responsive. So a proper tuning
5 of these properties for developing a metal free electrocatalyst by varying molecular architecture
6 and assembly makes the process challenging and demanding. To the best of our knowledge,
7 there is no report in literature which describes metal free hydrogen evolution from a covalent
8 organic framework.
9

10 Herein we have developed a 2D COF named SB-PORPy by the selection of two monomer units
11 with specific geometry under a homogeneous solution phase Schiff base condensation reaction.
12 The [2+2] condensation of D_{2h} and D_{4h} (**Figure 1**) type building blocks is geometrically and
13 topologically strained but the as synthesized material would be obtained in a crystalline form
14 with uniform pore size which is confirmed from the PXRD pattern. For the first time we have
15 focused on the electrochemical response of this pyrene-porphyrin comprised conjugated imine
16 based covalent organic framework (SB-PORPy) in order to understand the charge carrier
17 mobility of the metal free system having extensive π conjugation, pyrene core stimulated π - π
18 stacking and durability, coming from reticular assembly.
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40

41 **2. EXPERIMENTAL SECTION**

42 **2.1. Materials**

43 All reagents were supplied from commercial source and used without further purification.
44
45 5,10,15,20-Tetrakis(4-aminophenyl) porphyrin (TAP) was synthesized by previously reported
46 procedure⁴⁴ which is described in supporting information (**ESI Section S1**). 1,3,6,8-tetrakis(4-
47 formylphenyl) pyrene (TFFPy) was synthesized via new synthetic route for better yield. 1,3,6,8-
48 tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (Py-bpin₄) was synthesized
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 following the previously reported procedure⁴⁵. Tetrakis (triphenylphosphine) palladium (0), [1,1'-
4 Bis(diphenylphosphino)ferrocene]dichloropalladium(II) was received from sigma Aldrich. 4-
5 fromyl phenyl boronic acid, Dimethyl acetamide, o-dichlorobenzene etc. were purchased from
6 Spectrochem, India. Other solvents, acid, bases were supplied from local commercial source.
7
8
9
10
11

12 **2.2. Instrumentation.**

13
14
15 ¹H and ¹³C NMR were carried out using Bruker DPX-300 NMR spectrometer. Carbon, hydrogen
16 and nitrogen contents of SB-PORPy-COF by Perkin Elmer 2400 Series II CHN analyzer. X-Ray
17 powder diffraction patterns of the samples were obtained with a X'Pert PRO of PANalytical
18 diffractometer using Cu K α (= 0.15406 nm) radiation. Volumetric Nitrogen
19 adsorption/desorption analysis, Brunauer-Emmett-Teller (BET) specific surface area, pore
20 volume and micropore size etc were carried out at 77 K using Autosorb 1 (quantachrome,USA).
21 Prior to adsorption measurement the samples were outgassed in vacuum at 150 °C for 10 h.
22 NLDFT pore-size distribution was obtained from the adsorption/desorption isotherms by using
23 the carbon/slit-cylindrical pore model. The ¹³C cross-polarization magic angle spinning (CP-
24 MAS) NMR spectrum was obtained from 500MHz Bruker-Avance II spectrometer at a mass
25 frequency of 8 kHz. Thermogravimetry analysis (TGA) and differential thermal analyses (DTA)
26 of the samples are carried out in a TGA Instruments thermal analyzer TA-SDT Q-600. A Hitachi
27 S-5200 field-emission scanning electron microscope was used for the determination of the
28 morphology of the particles. Transmission electron microscopy (TEM) images were obtained by
29 a JEOL JEM 2010 transmission electron microscope operating at 100 kV. The samples were
30 prepared by dropping a colloidal solution onto the carbon-coated copper grids followed by
31 drying under high vacuum. The ¹H and ¹³C NMR spectra were obtained from Bruker AVANCE
32 III-400 MHz spectrometer. ¹H NMR spectra were collected at 400 MHz with chemical shift
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 referenced to the residual peak in CDCl₃ (δ : H 7.26ppm. Multiplicities are written as s (singlet),
4
5
6 d (doublet), t (triplet), m (multiplet) and br (broad).
7

8 All the electrochemical measurements were performed on a CHI 760E electrochemical work-
9
10 station with three electrode channels at room temperature. Three electrode set-up consists of a
11
12 glassy carbon (GC) as working electrode, platinum wire as counter and saturated calomel
13
14 electrode (SCE) as reference electrodes. The potentials measured were then corrected to the
15
16 reversible hydrogen electrode (RHE) using the following equation ($E_{\text{RHE}} = E_{\text{SCE}} + 0.241 + 0.059$
17
18 pH) V at room temperature. The electrolyte solution was deaerated by purging nitrogen gas into
19
20 the solution at least 30 min before each experiment. The scan rate used for all linear sweep
21
22 voltammetry study is 1 mV s⁻¹. The stability of the catalyst was determined by cyclic
23
24 voltammetry (CV) carried out between 0.2V and -0.5V (vs. RHE) at a scan rate of 100 mVs⁻¹ for
25
26 500 cycles. AC data obtained at -0.15V vs RHE with 5 mV ac amplitude in 0.5 (M) H₂SO₄. The
27
28 frequency range used for the impedance measurement is 100 kHz to 10 mHz.
29
30
31
32
33

34 **2.3. Synthesis of 1,3,6,8-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (Py-** 35 36 **bpin₄) (2)** 37

38 A schlenk tube was charged with 1.5 g 1,3,6,8-tetrabromopyrene **1** (2.9 mmol), bis (pinacolato)
39
40 diboron (4.4 g, 17.35 mmol), Pd(dppf)Cl₂ (0.175 g, 0.25 mmol) and potassium acetate (1.75 g,
41
42 17.85 mmol) in 15 ml anhydrous DMSO. The the mixture was backfilled with N₂ three times
43
44 and heated the reaction mixture at 90 °C for 48 h under stirring condition. The reaction mixture
45
46 was cooled to room temperature and extracted with Dichloromethane (DCM). The crude product
47
48 was isolated by solvent evaporation as a yellow solid. The crude was then purified by using flash
49
50 column chromatography on silica gel (60-120 mesh) using dichloromethane/toluene as an eluent.
51
52
53
54
55 The tetra borylated product **2** was isolated as grey solid (1.5 g, yield 76 %).
56
57
58
59
60

1
2
3 Mp: >300°C NMR: ¹H NMR (400 MHz, CDCl₃, ppm) 9.15 (s, 4H); 8.98 (s, 2H); 1.54 (s, 24H);
4
5 1.50 (s, 24H). ESI HRMS calcd (M+) 706.42115, found 706.419135. FTIR ν_{\max} (neat/cm⁻¹):
6
7 2928, 1552, 1341, 1210, 1142, 1086, 1018, 961, 858, 660.
8
9

10 11 12 13 14 **2.3. Synthesis of 1,3,6,8-tetrakis(4-formylphenyl) pyrene (TFFPy) (3)**

15
16 A mixture of 1,3,6,8-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (1.4 g, 2 mmol)
17
18 **2**, 4-bromo benzaldehyde (2.22 g, 12 mmol), palladium tetrakis(triphenylphosphine) (0.138 g,
19
20 0.12 mmol), and K₂CO₃ (1.6 g, 12 mmol) were placed in 20 ml dioxane/water mixture (16: 4).
21
22 The mixture was backfilled with nitrogen three times and stirred under nitrogen for 3 days at 90 °
23
24 C. The orange suspension reaction mixture was poured into ice water mixture. Then the yellow
25
26 solid was filtered, and washed with dilute HCl. The product was repeatedly washed with diethyl
27
28 ether (100 ml) and the product was dried in vacuum to give the 1,3,6,8-tetrakis(4-formylphenyl)
29
30 pyrene (TFFPy) **3** as yellowish-orange solid (1.11 g, 90%).
31
32

33
34 Mp: >300°C. NMR: ¹H NMR (400 MHz, CDCl₃, ppm) 10.16 (s, 4H); 8.18 (s, 4H); 8.09 (d, *J* =
35
36 8.0 Hz, 8H); 8.04 (s, 2H); 7.86 (d, *J* = 8.0 Hz, 8H). ESI HRMS calcd (M+) 618.18103, found
37
38 618.18010. FTIR ν_{\max} (neat/cm⁻¹): 3429, 2926, 2814, 2723, 1697, 1600, 1306, 1208, 831, 734.
39
40
41
42

43 44 **2.4. Synthesis of SB-PORPy-COF**

45
46 An dimethyl acetamide (DMAc)/ o-dichlorobenzene(o-DCB) (3.0/1.0 ml) mixture was added to
47
48 the mixture of 5,10,15,20-Tetrakis(4-aminophenyl)porphyrin (0.1 mmol, 67 mg) and 1,3,6,8-
49
50 tetrakis(4-formylphenyl) pyrene (0.1 mmol, 61 mg) using an acetic-acid catalyst (6 M, 0.5 ml)
51
52 in a schlenk tube (50 ml) and sonicated for 1h . Then the tube was degassed via three freeze–
53
54 pump–thaw cycles and flame sealed under vacuum and heated statically in oven at 120 °C for 7-
55
56 8 days. The greenish-brown precipitate was collected via centrifugation, washed Several times
57
58
59
60

1
2
3 with THF to remove the trapped guest molecules. The powder was collected and dried at 120 °C
4
5 under vacuum overnight to produce SB-PORPy-COF in an isolated yield of 76 %.
6
7

10 **2.5. Catalyst Preparation:**

11
12 Vulcan supported SB-PORPy-COF catalyst has been prepared by mechanical grinding with
13
14 Vulcan in 1:1 weight ratio. The catalyst ink was prepared by dispersing 2 mg of the composite
15
16 catalyst in 1 mL of mixed solvent solution (IPA: H₂O=1:1 v/v) and 20 μL of 0.5 wt% nafion
17
18 binder. The nafion binder (5 wt%) was diluted to 0.5 wt% with isopropyl alcohol (IPA). From
19
20 the prepared catalyst ink 10 μL was drop-casted on GC electrode (3 mm diameter) and dried
21
22 overnight in air. Before depositing the catalyst, the GC electrode was polished with 0.05 μm
23
24 alumina slurry, washed several times with distilled water.
25
26
27
28
29
30
31

32 **3. RESULT AND DISCUSSION**

33
34 In order to construct the crystalline SB-PORPy-COFs, we have selected tetra-armed 5,10,15,20-
35
36 tetrakis (4-aminophenyl) porphyrin (TAP) (**ESI Section S1**) of D_{4h} symmetry and 1,3,6,8-
37
38 tetrakis(4-formylphenyl) pyrene (TFFPy) (**compound 3, Figure 1A**) of D_{2h} symmetry as the
39
40 starting building block. The acid catalyzed reversible solvothermal condensation between TAP
41
42 and TFFPy (**Figure 1B**) in the solvent mixture of dimethylacetamide/ o-dichlorobenzene (3:1 by
43
44 vol.) using 6(M) acetic acid under static heating at 120 °C for 7 days produced SB-PORPy-COF
45
46 as a greenish-brown powder which is insoluble in common organic solvents and even in strong
47
48 inorganic acids and bases such as aqueous H₂SO₄ and NaOH. At first the COF synthesis had
49
50 been optimized using different solvent system such as Mesitylene/Dioxane, dimethyl formamide,
51
52 o-dichlorobenzene, Dioxane/n-Butanol and N,N dimethyl acetamide/o-dichlorobenzene
53
54
55
56
57
58
59
60

1
2
3 maintaining same molar ratio (1:1) of two monomers. Among those, the N,N dimethyl
4 acetamide/o-dichlorobenzene solvent system was the best trial for obtaining the moderate surface
5 area along with significant crystallinity. The extensive formation of imine linkage was detected
6 by Fourier transform Infrared (FT-IR) and ^{13}C cross polarized (CP) solid state MAS NMR
7 spectroscopic methods. It has been clearly seen that In FT-IR spectra (**Figure 2A**) the absorption
8 band near 1601 cm^{-1} for the C=N bond stretching modes which states about the existence of
9 imine functionality between the pyrene and porphyrin moiety. The structural integrity of the
10 framework was confirmed by solid state CP-MAS NMR which displays the resonance signal
11 around 159.7 ppm for the carbon of C=N bond (**Figure 2B**). The resonance peak around ~ 147.1
12 ppm can be assigned to the quaternary carbon of the organic framework. The peak around ~ 119.6
13 ppm is indicative of the methine carbon of the porphyrin macrocycle and at ~ 114.1 ppm for β -
14 pyrrolic carbon. The biggest resonance peak around ~ 131.1 ppm is mainly due to the pyrenyl
15 phenyl moiety of the covalent organic framework. The X-ray photo-electron spectroscopy (XPS)
16 of SB-PORPy-COF had shown the broad peak centered around 399 eV which can be attributed
17 to the $\text{N}_{1\text{S}}$ and the peak around 284 eV which is for $\text{C}_{1\text{S}}$. The connectivity between the pyrene
18 and porphyrin moiety via C=N bond formation, is directly reflected to deconvoluted $\text{N}_{1\text{S}}$ spectra
19 which is composed of three component peaks. The first, second and third component peaks are at
20 398, 399 and 400 eV respectively. The first peak (398 eV) is mainly due to presence pyrrolic
21 nitrogen and pyrrolic -NH peak is present at the slight shifted higher binding energy region (400
22 eV) (**Figure 2C&D**). The 'N' atom associated with Schiff base bond (C=N) has shown the peak
23 at 399 eV. The morphological analysis and porosity of SB-PORPy-COF has been investigated
24 using scanning electron microscopy (SEM) (**figure 4D**) and high resolution transmission
25 electron microscopy (HRTEM) respectively. Those revealed that SB-PORPy is composed of 80-
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 150 nm sized porous thin platelets with granular morphology respectively which has been shown
4 in **Figure 2E & 2F** (HRTEM). The SB-PORPy COF has shown promising thermal stability upto
5
6 400 °C which was confirmed by the thermo gravimetric (TGA) analysis (ESI, **Fig S1**).
7
8

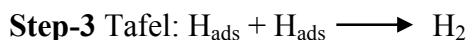
9
10 The possible crystal structure of the SB-PORPy-COF was obtained by the experimental XRD
11 measurements along with theoretical structural simulations. The molecular assembly will be
12 slightly topologically strained due to the geometries (D_{2h} and D_{4h}) of monomers. But the static
13 heating of reaction mixture for long time (7 days) has made the SB-PORPy-COF crystalline. The
14 strong XRD peaks at the position $2\theta = 4.9^\circ$ and $\sim 22^\circ$ which can be assigned to the (020), and
15 (202) facets respectively. The hump centered at $\sim 22^\circ$ may be attributed to zigzag π - π stacking of
16 2D layers. The theoretical PXRD pattern of AA stacking model (black, **Figure 3B**) of SB-
17 PORPy monolayers is in perfect agreement with the peak position and the intensity of the
18 experimental obtained PXRD (blue, **Figure 3A**), whereas the AB stacking model (red, **Figure**
19 **3C**) is totally different. The theoretical quasi 2D eclipse structure (AA) and the staggered
20 structure (AB) has shown in the **figure 3D & 3E**. The PXRD data obtained after Pawley
21 refinement resulted (**Figure 3F**, blue curve) in a pattern that is exactly matching with the
22 experimentally observed pattern (purple scattered asterisk, showing small difference **Figure 3F**,
23 wine plot) giving the Pawley refinement factor (R_p) $\sim 2.79\%$. A 3D triclinic unit cell (P_1 space
24 group) having the parameters of $a = 37.098 \text{ \AA}$, $b = 36.8016 \text{ \AA}$, $c = 8.06797 \text{ \AA}$, $\alpha = 89.9333^\circ$, $\gamma =$
25 89.9038° and $\beta = 90.1005^\circ$ was derived from the theoretical optimization of SB-PORPy-COF
26 (ESI **Section S4**). The absence of long range periodicity can be attributed to the fact that
27 geometry of two building blocks (D_{2h} & D_{4h}) are slightly topologically overruled to give a strain
28 free periodic structure. The permanent porosity of SB-PORPy-COF has been determined by
29 measuring volumetric N_2 adsorption/desorption experiment at 77 K which exhibits type-I
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 isotherm which is the characteristic of intrinsic microporosity of COF SB-PORPy (**Figure 4A**).
4
5 The Brunauer-Emmett-Teller surface area and the total pore volume are $\sim 869 \text{ m}^2 \text{ g}^{-1}$ and 0.51
6
7 $\text{cm}^3 \text{ g}^{-1}$. The sample was activated at 160°C to remove the solvent molecule from the lattice for
8
9 sorption analysis. The pore size distribution based on non-local density functional theory has
10
11 shown an unimodal porosity having single peak at 1.7 nm (**Figure 4B**). The stability test of the
12
13 SB-PORPy-COF material had been done by emerging the powder sample in various organic
14
15 solvents such as THF, dioxane, toluene, DMF etc. for 7 days. There was no change of powder
16
17 XRD pattern had been observed after solvent soaking for 7 days. The material had shown the
18
19 remarkable stability in aqueous, acidic (0.5 M) or alkaline (0.5 M) solution (**Figure 4C**). In this
20
21 porous framework, the pyrene core is connected to the porphyrin moiety alternatively through
22
23 the C=N linkage which creates the fluorescent channel in the 2D COF. The electronic absorption
24
25 spectrum has shown a solid state broad absorption giving three maxima in the visible region. The
26
27 maxima centered at 663 nm may be attributed to the α -Q band, 570 nm for β -Q band and 400 nm
28
29 is for sorbet band of porphyrin unit present in the framework. The COF has the strong
30
31 photoluminescence emission giving maxima at 688 nm (ESI, **Figure S2**).
32
33
34
35
36
37
38
39
40
41

42 **3.1. Metal free electrochemical hydrogen evolution**

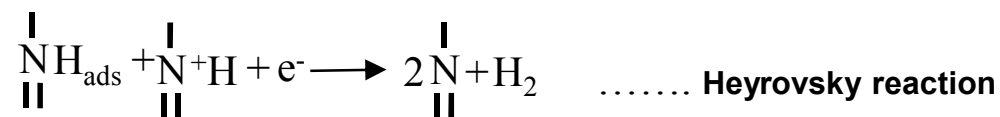
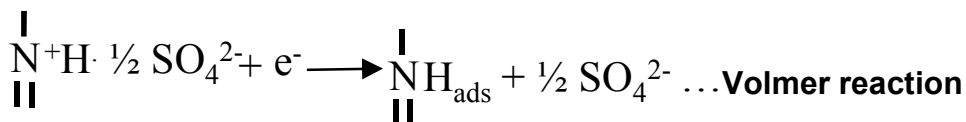
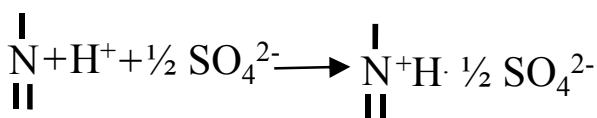
43
44 Electrochemical activities of SB-PORPy-COF catalyst toward HER was investigated in 0.5 (M)
45
46 H_2SO_4 solution. So, far hydrogen evolution catalyzed by any type of transition metal based
47
48 complexes and materials in previous report, but electrocatalytic hydrogen evolution by any type
49
50 of metal free COF has never been reported. A few cobalt complexes including cobalt porphyrin
51
52 were testified to be an effective electrocatalyst for electrocatalytic HER⁴⁶⁻⁴⁸. However, very high
53
54 overpotentials were required for such systems. In general, only COFs have been used to support
55
56
57
58
59
60

1
2
3 the porosity and large surface area for the electrocatalysts^{49,50} An efficient electrocatalysts can
4 also be developed through rational designing of COFs.⁵¹ In the following study, SB-PORPy COF
5 had shown to be an efficient metal free electrocatalyst with a remarkably low onset overpotential
6 of ~50 mV which is the lowest reported overpotential ever for any types of COFs (**Figure 5A**) in
7 acidic solution. From the linear sweep voltammetry curve, it is clear that the electro-catalytic
8 activities of bare glassy carbon (GC) and Vulcan were negligibly small. HER as reflected by low
9 current density and very high overpotential for pure Vulcan (red curve, **Figure 5A**) whereas
10 Vulcan/COF/GC represents a much larger current density with extremely low overpotential for
11 HER (black curve, **Figure 5A**). This was the indication of a pronounced electro-activity of the as
12 synthesized SB-PORPy-COF. This result clearly indicates that principal contribution towards
13 HER comes from as synthesized SB-PORPy-COF and confirms about it's electro-activity
14 towards hydrogen evolution reaction. The conductive Vulcan carbon has only been used to
15 enhance the conductivity of the system. The potential to achieve 1 mA/cm² was found to be -
16 0.2V vs RHE which is better than any cobalt based COF systems. More interestingly,
17 overpotential required for 5 mA cm⁻² exchange current density is as low as 380 mV indicating
18 extraordinary activity towards hydrogen evolution reaction in terms of COF based systems. HER
19 mechanism can be well-reflected from the Tafel slope involving the following three steps
20 occurring on the catalyst surface.
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44



54
55 Step 1 is the adsorption step and desorption step on porous surface of electrocatalyst. H₂
56 evolution can happen either through Step 2 (Heyrovsky) or Step 3 (Tafel). Therefore, total H₂
57
58
59
60

1
2
3 evolution reaction will happen either following Volmer-Heyrovsky or Volmer-Tafel mechanism.
4
5 A Tafel slope value of 30 mV/dec will indicates rate determining step (r.d.s.) to be Tafel whereas
6
7 40 mV/dec and 120 mV/dec will respectively indicate Heyrovsky and Volmer will be the r.d.s.⁵²⁻
8
9
10
11 ⁵⁵.The linear nature of the Tafel slope obtained from the polarization curve was $\sim 116 \text{ mV.dec}^{-1}$
12
13 indicating Volmer-Heyrovsky mechanism for the HER on the SB-PORPy COF surface and the
14
15 Volmer step is the rate determining step (**Figure 5B**). The imine nitrogen sites present in the
16
17 COF (-N=) are considered as free docking sites for HER. In acidic solution, imine nitrogen
18
19 atoms are protonated making the moiety positively charged hyperporphyrinic structure whereas
20
21 SO_4^{2-} maintains the electro-neutrality. On the other hand, H-H combination occurred with the
22
23 help of other adjacent imine nitrogen sites facilitating the hydrogen evolution process from the
24
25 surface (**Figure 6**).
26
27
28
29
30



31
32
33
34
35
36
37
38
39
40
41
42
43
44 A general scheme can be considered from the electrochemical impedance spectroscopy which is
45
46 a useful tool for studying the electrode kinetics in HER. **Figure 5C** represents Nyquist plot of
47
48 SB-PORPy-COF catalyst in the frequency range 100 kHz to 10 MHz at -0.15V vs RHE in 0.5 M
49
50 H_2SO_4 solution. As evident from **Figure 5C**, only one semicircle was observed with no
51
52 prominent Warburg impedance indicating kinetically controlled electrochemical reaction on
53
54 electrode surface due to rapid ionic transportation in the electrolyte. The diameter of the
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

semicircle can be attributed to the charge-transfer resistance (R_{ct}). A low value of R_{ct} corresponds to the fast reaction kinetics on the catalyst surface. The SB-PORPy-COF catalyst showed a very small value of R_{ct} ($\sim 145 \Omega$) (**Figure. 5C**). One of the concerns of the HER catalysts is stability, many catalysts lose their activity after a few cycles. To evaluate the durability of the SB-PORPy-COF catalyst, a potential cycling was conducted in the potential range 0.2V to -0.5V vs RHE at a scan rate of 100 mVs^{-1} for 500 cycles. As shown in **Figure 5D**, there is almost no loss of activity observed in terms of both onset potential and current density at different potentials, indicating good stability of the catalyst in acidic solution. The XPS had been done for N_{1s} to investigate the chemical state of nitrogen atoms (pyrrolic N and Schiff base N) which was remained intact after 500 cycles which accounts about the promising stability in 0.5 (M) H_2SO_4 (**ESI Figure S3**). The Faradaic efficiency (FE) of SB-PORPy-COF was evaluated to be 90 % which accounts about the purity of catalyst towards electrochemical hydrogen evolution (**ESI Figure S4, section S3**). The FE value is quite comparable to the other established electrocatalysts⁵⁶.

CONCLUSION

In summary, we have designed an imine based conjugated pyrene, porphyrin comprised microporous quasi-2D covalent organic framework. The reversibility of imine bond formation leads to the formation of thermodynamically controlled crystalline framework in spite of the topological restriction from the view point of molecular geometry. A π electronic conjugation between pyrene and porphyrin creates a conducting channel (AA stacking). We have investigated the charge carrier mobility and metal free hydrogen evolution by imposing some short of electrochemical stimulation on SB-PORPy-COF. As far as we know, till date there is no COF based catalyst known that enables metal free hydrogen evolution. Such COFs are stable

1
2
3 even in strongly acidic/alkaline conditions. Furthermore such topologically strained crystalline
4
5 imine based covalent organic frameworks will increase the structural diversity of these (COFs)
6
7
8 classes of materials and find abundant scope of utility and applicability to understand the
9
10 electrochemical aspects of COFs.
11

12 **ASSOCIATED CONTENT**

13 **Supporting Information**

14
15
16 The Supporting Information (ESI) is available free of charge on the ACS Publications website.
17
18
19 Synthetic procedures, IR, melting point, ¹H NMR, DTA- TGA, UV-vis, Photo luminescence,
20
21 N1s XPS for stability, Faradaic efficiency and theoretical simulations are available in ESI.
22
23
24

25 **AUTHOR INFORMATION**

26 **Corresponding Author**

27
28
29
30
31
32 *Prof. S. Bhattacharya, Email. director@iacs.res.in
33

34
35 *Dr. A. Pradhan, Email. msap5@iacs.res.in
36

37
38 *Prof. A. Bhaumik, Email. msab@iacs.res.in
39

40
41
42
43
44 *Dr. M. Addicoat, Email. matthew.addicoat@ntu.ac.uk
45

46 **Author Contributions**

47
48 ^{||} Both author contributed equally.
49

50
51 The manuscript was written through contributions of all authors. All authors have given approval
52
53 to the final version of the manuscript.
54

55 **Notes**

1
2
3 The authors declare no competing financial interest.
4
5

6 7 **ACKNOWLEDGMENT**

8
9 SB, SKD thank CSIR and UGC respectively for funding. AP acknowledges DST for funding
10 through INSPIRE program. Prof. SB acknowledges support received from DST (J. C. Bose
11 fellowship) and that from DRU at IACS. AB thanks DST for instrumental supports through DST
12 Unit on Nanoscience. SCP & RKJ thanks DST for financial support.
13
14
15
16
17

18 19 **REFERENCES**

- 20
21
22 (1) Xu, H.; Gao, J.; Jiang, D. Stable, Crystalline, Porous, Covalent Organic Frameworks as a
23 Platform for Chiral Organocatalysts. *Nat. Chem.* **2015**, *7*, 905-912.
24
25 (2) Dalapati, S.; Addicoat, M.; Jin, S.; Sakurai, T.; Gao, J.; Xu, H.; Irle, S.; Seki, S.;
26 Jiang, D. Rational Design of Crystalline Supermicroporous Covalent Organic
27 Frameworks with Triangular Topologies. *Nat. Commun.* **2015**, *6*, 7786 doi:
28 10.1038/ncomms8786.
29
30 (3) Liu, Y.; Ma, Y.; Zhao, Y.; Sun, X.; Gándara, F.; Furukawa, H.; Liu, Z.; Zhu, H.; Zhu, C.;
31 Suenaga, K.; Oleynikov, P.; Alshammari, A. S.; Zhang, X.; Terasaki, O.; Yaghi, O. M.
32 Weaving of Organic Threads into a Crystalline Covalent Organic Framework. *Science*
33 **2016**, *351*, 365-369.
34
35 (4) Huang, N.; Ding, X.; Kim, J.; Ihee, H.; Jiang, D. A Photoresponsive Smart Covalent
36 Organic Framework. *Angew. Chem. Int. Ed.* **2015**, *54*, 8704-8707.
37
38 (5) Kandambeth, S.; Biswal, B. P.; Chaudhari, H. D.; Rout, K. C.; H., S. K.; Mitra, S.; Karak,
39 S.; Das, Mukherjee, A. R.; Kharul, U. K.; Banerjee, R. Selective Molecular Sieving in
40 Self-standing Porous Covalent Organic Framework Membranes. *Adv. Mater.* **2017**, *29*,
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 1603945.
4
5
6 (6) Bojdys, M. J.; Jeromenok, J.; Thomas, A.; Antonietti, M. Rational Extension of the
7
8 Family of Layered, Covalent, Triazine-Based Frameworks with Regular Porosity. *Adv.*
9
10 *Mater.* **2010**, *22*, 2202-2205.
11
12 (7) Tang, J.; Yamauchi, Y. Carbon materials: MOF Morphologies in Control. *Nat. Chem.*
13
14 **2016**, *8*, 638-639.
15
16 (8) Salunkhe, R. R.; Young, C.; Tang, J.; Takei, T.; Ide, Y.; Kobayashi, N.; Yamauchi, Y. A
17
18 High-Performance Supercapacitor Cell Based on ZIF-8-Derived Nanoporous Carbon
19
20 using an Organic Electrolyte. *Chem. Commun.* **2016**, *52*, 4764-4767.
21
22 (9) Salunkhe, R. R.; Kamachi, Y.; Torad, N. L.; Hwang, S. M.; Sun, Z. Q.; Dou, S. X.; Kim,
23
24 J. H.; Yamauchi, Y. Fabrication of Symmetric Supercapacitors Based on MOF-Derived
25
26 Nanoporous Carbons. *J. Mater. Chem. A* **2014**, *2*, 19848-19854.
27
28
29
30
31 (10) Rabbani, M. G.; Sekizkardes, A. K.; Kahveci, Z.; Reich, T. E.; Ding, R. E.; El-Kaderi, H.
32
33 M. A 2D Mesoporous Imine-Linked Covalent Organic Framework for High Pressure Gas
34
35 Storage Applications. *Chem. Eur. J.* **2013**, *19*, 3324-3328.
36
37 (11) Shan, M.; Seoane, B.; Rozhko, E.; Dikhtiarenko, A.; Clet, G.; Kapteijn, F.; Gascon, J.
38
39 Azine-Linked Covalent Organic Framework (COF)-Based Mixed-Matrix Membranes for
40
41 CO₂/CH₄ Separation. *Chem. Eur. J.* **2016**, *22*, 14467-14470.
42
43 (12) Huang, N.; Chen, X.; Krishna, R.; Jiang, D. Two-Dimensional Covalent Organic
44
45 Frameworks for Carbon Dioxide Capture through Channel-Wall Functionalization.
46
47 *Angew. Chem. Int. Ed.* **2015**, *54*, 2986-2990.
48
49 (13) Furukawa, F.; Yaghi, O. M. Storage of Hydrogen, Methane, and Carbon Dioxide in
50
51 Highly Porous Covalent Organic Frameworks for Clean Energy Applications. *J. Am.*
52
53
54
55
56
57
58
59
60

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- Chem. Soc.*, **2009**, *131*, 8875-8883.
- (14) Li, X. D.; Zang, H. P.; Wang, J. T.; Wang, J. F.; Zhang, H. Design of Tetraphenyl Silsesquioxane Based Covalent-Organic Frameworks as Hydrogen Storage Materials. *J. Mater. Chem. A* **2014**, *2*, 18554-18561.
- (15) Shi, X.; Yao, Y.; Xu, Y.; Liu, K.; Zhu, G.; Chi, L.; Lu, G. Imparting Catalytic Activity to a Covalent Organic Framework Material by Nanoparticle Encapsulation. *ACS Appl. Mater. Interfaces* **2017**, *9*, 7481-7488.
- (16) Shinde, D. B.; Kandambeth, S.; Pachfule, P.; Kumar, R. R.; Banerjee, R. Bifunctional Covalent Organic Frameworks with Two Dimensional Organocatalytic Micropores. *Chem. Commun.* **2015**, *51*, 310-313.
- (17) Peng, Y.; Hu, Z.; Gao, Y.; Yuan, D.; Kang, Z.; Qian, Y.; Yan, N.; Zhao, D. Synthesis of a Sulfonated Two-Dimensional Covalent Organic Framework as an Efficient Solid Acid Catalyst for Biobased Chemical Conversion. *ChemSusChem*. **2015**, *8*, 3208-3212.
- (18) Xu, H.; Chen, X.; Gao, J.; Lin, J.; Addicoat, M.; Irle, S.; Jiang, D. Catalytic Covalent Organic Frameworks via Pore Surface Engineering. *Chem. Commun.* **2014**, *50*, 1292-1294.
- (19) Li, P. -Z.; Wang, X. -J.; Liu, J.; Lim, J. S.; Zou, R.; Zhao, Y. A Triazole-Containing Metal-Organic Framework as a Highly Effective and Substrate Size-Dependent Catalyst for CO₂ Conversion. *J. Am. Chem. Soc.* **2016**, *138*, 2142-2145.
- (20) Fang, Q.; Wang, J.; Gu, S.; Kaspar, R. B.; Zhuang, Z.; Zheng, J.; Guo, H.; Qiu, S.; Yan, Y. 3D Porous Crystalline Polyimide Covalent Organic Frameworks for Drug Delivery. *J. Am. Chem. Soc.* **2015**, *137*, 8352-8355.
- (21) Bai, L.; Phua, S. Z. F.; Lim, W. Q.; Jana, A.; Luo, Z.; Tham, H. P.; Zhao, L.; Gao, Q.;

- 1
2
3 Zhao, Y. Nanoscale Covalent Organic Frameworks as Smart Carriers for Drug Delivery.
4
5 *Chem. Commun.* **2016**, *52*, 4128-4131.
6
7
8 (22) Vyas, V. S.; Vishwakarma, M.; Moudrakovski, I.; Haase, F.; Savasci, G.; Ochsenfeld, C.;
9
10 Spatz, J. P.; Lotsch, B. V. Exploiting Noncovalent Interactions in an Imine-Based
11
12 Covalent Organic Framework for Quercetin Delivery. *Adv Mater.* **2016**, *28*, 8749-8754.
13
14
15 (23) Wan, S.; Gándara, F.; Asano, A.; Furukawa, H.; Saeki, A.; Dey, S. K.; Liao, L.;
16
17 Ambrogio, M. W.; Botros, Y. Y.; Duan, X.; Seki, S.; Stoddart, J. F.; Yaghi, O. M.
18
19 Covalent Organic Frameworks with High Charge Carrier Mobility. *Chem.*
20
21 *Mater.* **2011**, *23*, 4094-4097.
22
23
24 (24) Ding, X.; Guo, J.; Feng, X.; Honsho, Y.; Guo, J.; Seki, S.; Maitarad, P.; Saeki, A.;
25
26 Nagase, S.; Jiang, D. Synthesis of Metallophthalocyanine Covalent Organic Frameworks
27
28 That Exhibit High Carrier Mobility and Photoconductivity. *Angew. Chem. Int. Ed.* **2011**,
29
30 *50*, 1289-1293.
31
32
33
34 (25) He, T.; Pachfule, P.; Wu, H.; Xu, Q.; Chen, P. Hydrogen Carriers. *Nat. Rev. Mater.* **2016**,
35
36 *1*, 16059.
37
38
39 (26) Yang, H.; Zhang, S.; Han, L.; Zhang, Z.; Xue, Z.; Gao, J.; Li, Y.; Huang, C.; Yi,
40
41 Y.; Liu, H.; Li, Y. High Conductive Two-Dimensional Covalent Organic Framework for
42
43 Lithium Storage with Large Capacity. *ACS Appl. Mater. Interfaces* **2016**, *8*, 5366-5375.
44
45
46 (27) Cai, S. L.; Zhang, Y. B.; Pun, A. B.; He, B.; Yang, J.; Toma, F. M.; Sharp, I. D.; Yaghi,
47
48 O. M. Fan, J.; Zheng, S. R.; Zhang, W. G.; Liu, Y. Tunable Electrical Conductivity in
49
50 Oriented Thin Films of Tetrathiafulvalene-Based Covalent Organic Framework. *Chem.*
51
52 *Sci.* **2014**, *5*, 4693-4700.
53
54
55 (28) Nath, B.; Li, W.-H.; Huang, J. -H.; Wang, G. -E.; Fu, Z. -H.; Yao, M. -S.; Xu, G. A New
56
57
58
59
60

- 1
2
3 Azodioxy-linked Porphyrin-Based Semiconductive Covalent Organic Framework with I₂
4 Doping-Enhanced Photoconductivity. *CrystEngComm*. **2016**, *18*, 4259-4263.
5
6
7
8 (29) Smith, B. J.; Hwang, N.; Chavez, A. D.; Novotney J. L.; Dichtel, W. R. Growth Rates
9 and Water Stability of 2D Boronate Ester Covalent Organic Frameworks. *Chem.*
10
11
12 *Commun*. **2015**, *51*, 7532-7535.
13
14
15 (30) Medina, D. D.; Werner, V.; Auras, F.; Tautz, R.; Dogru, M.; Schuster, J.; Linke, S.;
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- (31) Wang, P.; Wu, Q.; Han, L.; Wang, S.; Fang, S.; Zhang, Z.; Sun, S. Synthesis of
Conjugated Covalent Organic Frameworks/Graphene Composite for Supercapacitor
Electrodes. *RSC Adv*. **2015**, *5*, 27290-27294.
- (32) Patra, B. C.; Khilari, S.; Satyanarayana, L.; Pradhan, D.; Bhaumik, A. A New
Benzimidazole Based Covalent Organic Polymer Having High Energy Storage Capacity.
Chem. Commun. **2016**, *52*, 7592-7595.
- (33) Huang, Y. B.; Pachfule, P.; Sun, J. K.; Xu, Q. From Covalent–Organic Frameworks to
Hierarchically Porous B-doped Carbons: A Molten-Salt Approach. *J. Mater. Chem. A*
2016, *4*, 4273-4279.
- (34) Lin, G.; Ding, H.; Yuan, D.; Wang, B.; Wang C. A Pyrene-Based, Fluorescent Three-
Dimensional Covalent Organic Framework. *J. Am. Chem. Soc.* **2016**, *138*, 3302-3305.
- (35) Dalapati, S.; Jin, E.; Addicoat, M.; Heine, T.; Jiang, D. Highly Emissive Covalent
Organic Frameworks. *J. Am. Chem. Soc.* **2016**, *138*, 5797-5800.
- (36) Neti, V. S. P. K.; Wu, X.; Deng, S.; Echegoyen L. Synthesis of a Phthalocyanine and
Porphyrin 2D Covalent Organic Framework. *CrystEngComm*. **2013**, *15*, 6892-6895.

- 1
2
3 (37) Lin, S.; Diercks, C. S.; Zhang, Y. B.; Kornienko, N.; Nichols, E. M.; Zhao, Y.; Paris, A.
4
5 R.; Kim, D.; Yang, P.; Yaghi, O. M.; Chang, C. J. Covalent Organic Frameworks
6
7 Comprising Cobalt Porphyrins for Catalytic CO₂ Reduction in Water. *Science* **2015**, *349*,
8
9 1208-1213.
10
11
12 (38) Dalapati, S.; Jin, S.; Gao, J.; Xu, Y.; Nagai, A.; Jiang, D. An Azine-Linked Covalent
13
14 Organic Framework. *J. Am. Chem. Soc.* **2013**, *135*, 17310-17313.
15
16
17 (39) Bertrand, G. H. V.; Michaelis, V. K.; Ong, T. C.; Griffin, R. G.; Dincă, M. Thiophene-
18
19 Based Covalent Organic Frameworks. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 4923-
20
21 4928.
22
23
24 (40) Ascherl, L.; Sick, T.; Margraf, J. T.; Lapidus, S. H.; Calik, M.; Hettstedt, C.;
25
26 Karaghiosoff, K.; Döblinger, M.; Clark, T.; Chapman, K. W.; Auras, F.; Bein, T.
27
28 Molecular docking sites designed for the generation of highly crystalline covalent organic
29
30 frameworks. *Nat. Chem.* **2016**, *8*, 310-316.
31
32
33 (41) Stegbauer, L.; Schwinghammer, K.; Lotsch, B. V. A hydrazone-based covalent organic
34
35 framework for photocatalytic hydrogen production. *Chem. Sci.* **2014**, *5*, 2789-2793.
36
37
38 (42) Gao, G.; Jiao, Y.; Waclawik, E. R.; Du, A. Single Atom (Pd/Pt) Supported on Graphitic
39
40 Carbon Nitride as an Efficient Photocatalyst for Visible-Light Reduction of Carbon
41
42 Dioxide. *J. Am. Chem. Soc.* **2016**, *138*, 6292-6297.
43
44
45 (43) Kaeffer, N.; Morozan, A.; Fize, J.; Martinez, E.; Guetaz, L.; Artero, V. The Dark Side
46
47 of Molecular Catalysis: Diimine-Dioxime Cobalt Complexes Are Not the Actual
48
49 Hydrogen Evolution Electrocatalyst in Acidic Aqueous Solutions. *ACS Catal.* **2016**, *6*,
50
51 3727-3737.
52
53
54 (44) Xue, Z.; Lee, P. P. S.; Wang, Y.; Kwong, D. W. J.; Li, J.; Xin, J. H.; Wong, W.-K.;
55
56
57
58
59
60

- 1
2
3 Cheuk, K. K.L. Further Insight into Aryl Nitration of Tetraphenylporphyrin. *Tetrahedron*
4
5 **2011**, *67*, 6030-6035.
6
7
8 (45) Sprick, R. S.; Jiang, J.-X.; Bonillo, B.; Ren, S.; Ratvijitvech, T.; Guiglion,
9 P.; Zwijnenburg, M. A.; D. J. Adams; Cooper, A. I. Tunable Organic Photocatalysts for
10 Visible-Light-Driven Hydrogen Evolution. *J. Am. Chem. Soc.* **2015**, *137*, 3265-3270.
11
12
13 (46) Fan, Z.; Luo, Z.; Huang, X.; Li, B.; Chen, Y.; Wang, J.; Hu, Y.; Zhang, H. Synthesis of
14 4H/*fcc* Noble Multimetallic Nanoribbons for Electrocatalytic Hydrogen Evolution
15 Reaction. *J. Am. Chem. Soc.* **2016**, *138*, 1414-1419.
16
17
18 (47) Kamire, R. J.; Majewski, M. B.; Hoffeditz, W. L.; Phelan, B. T.; Farha, O. K. ; Hupp , J.
19 T.; Wasielewski, M. R. Photodriven Hydrogen Evolution by Molecular Catalysts using
20 Al₂O₃-Protected Perylene-3,4-Dicarboximide on NiO Electrodes. *Chem. Sci.* **2017**, *8*,
21 541-549.
22
23
24 (48) Huang, D.; Lu, J.; Li, S.; Luo, Y.; Zhao, C.; Hu, B.; Wang, M.; Shen, Y. Fabrication of
25 Cobalt Porphyrin. Electrochemically Reduced Graphene Oxide Hybrid Films for
26 Electrocatalytic Hydrogen Evolution in Aqueous Solution. *Langmuir* **2014**, *30*, 6990-
27 6998.
28
29
30 (49) Aiyappa, H. B.; Thote, J.; Shinde, D.B.; Banerjee, R.; Kurungot, S. Cobalt-Modified
31 Covalent Organic Framework as a Robust Water Oxidation Electrocatalyst. *Chem. Mater.*
32 **2016**, *28*, 4375-4379
33
34
35 (50) Ma, W.; Yu, P.; Ohsaka, T.; Mao, L. An Efficient Electrocatalyst for Oxygen Reduction
36 Reaction Derived from a Co-porphyrin-based Covalent Organic Framework.
37 *Electrochem. Commun.* **2015**, *52*, 53-57.
38
39
40
41
42 (51) Lin, C. -Y.; Zhang, L.; Zhao, Z.; Xia, Z. Design Principles for Covalent Organic
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 Frameworks as Efficient Electrocatalysts in Clean Energy Conversion and Green Oxidizer
4
5 Production. *Adv. Mater.* **2017**, *29*, 1606635.
6
7
8 (52) Gruba, Z.; Hukovic, M. M.; Babic, R.; Nanocrystalline and Coarse Grained
9 Polycrystalline Nickel Catalysts for the Hydrogen Evolution Reaction. *Int. J. Hydrogen*
10 *Energy* **2013**, *38*, 4437-444.
11
12
13 (53) Huang, D.; Lu, J.; Li, S.; Luo, Y.; Zhao, C.; Hu, B.; Wang, M.; Shen, Y. Fabrication of
14 Cobalt Porphyrin. Electrochemically Reduced Graphene Oxide Hybrid Films for
15 Electrochemical Hydrogen Evolution in Aqueous Solution. *Langmuir* **2014**, *30*, 6990-
16 6998.
17
18
19 (54) Lv, H.; Xi, Z.; Chen, Z.; Guo, S.; Yu, Y.; Zhu, W.; Li, Q.; Zhang, X.; Pan, M.;
20 Lu, G.; Mu, S.; Sun, S. A New Core/Shell NiAu/Au Nanoparticle Catalyst with Pt-like
21 Activity for Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2015**, *137*, 5859-5862.
22
23
24 (55) Pentland, N.; Bockris, J. O. M.; Sheldon, E. Hydrogen Evolution Reaction on Copper,
25 Gold, Molybdenum, Palladium, Rhodium, and Iron. *J. Electrochem. Soc.* **1957**, *104*, 182-
26 194.
27
28
29 (56) Vrabel, H.; Hu, X. Molybdenum Boride and Carbide Catalyze Hydrogen Evolution in
30 both Acidic and Basic Solutions. *Angew. Chem. Int. Ed.* **2012**, *124*, 12875-12878.
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Figure 1

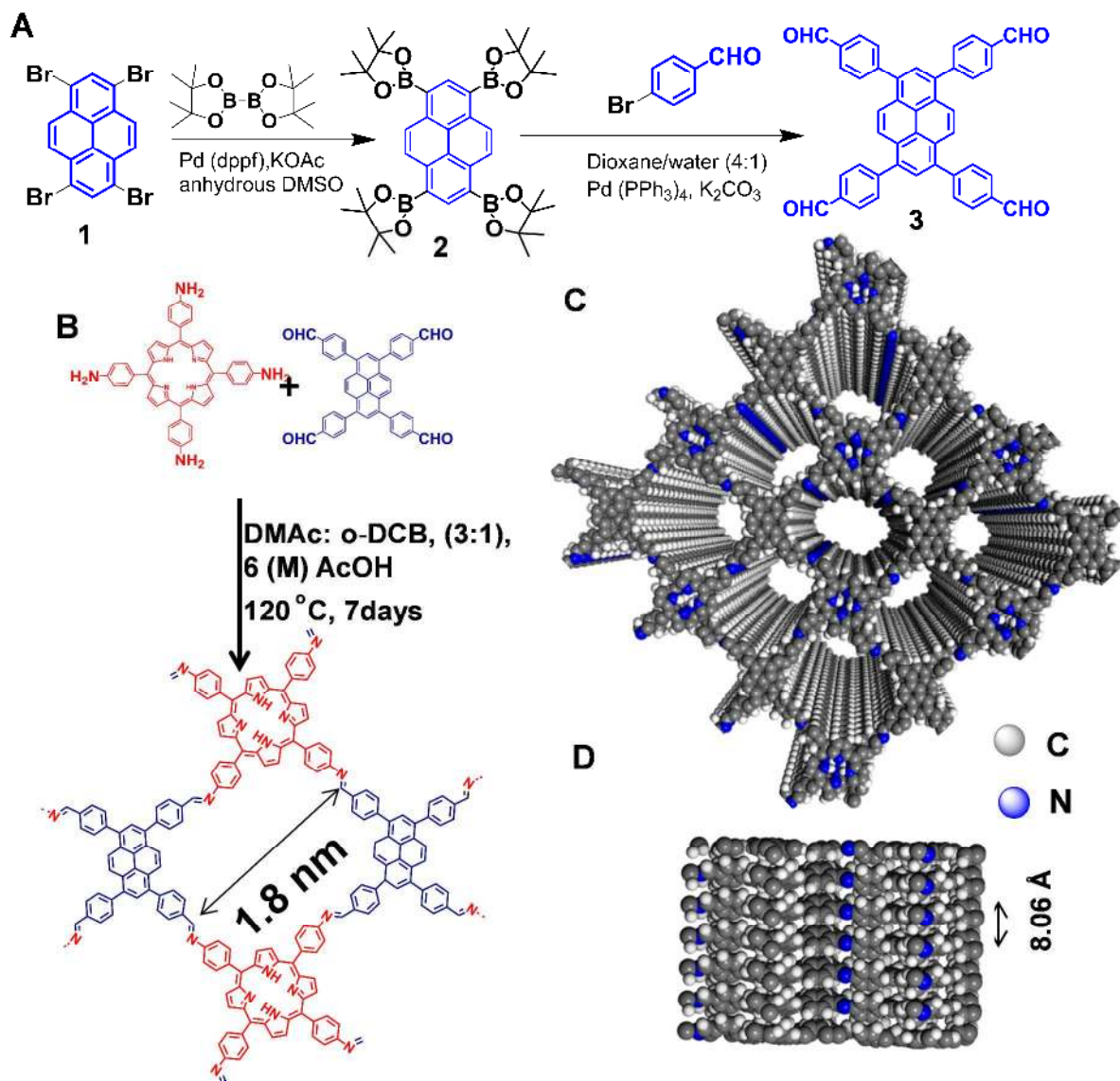


Figure 1. (A) Synthesis of 1,3,6,8-tetrakis(4-formylphenyl) pyrene (TFFPy) (B) Synthetic scheme of the imine based COF (SB-PORPy). (C) Top view (D) Side view of AA (eclipsed) stacking of SB-PORPy COF (gray: carbon, blue: nitrogen)

Figure. 2

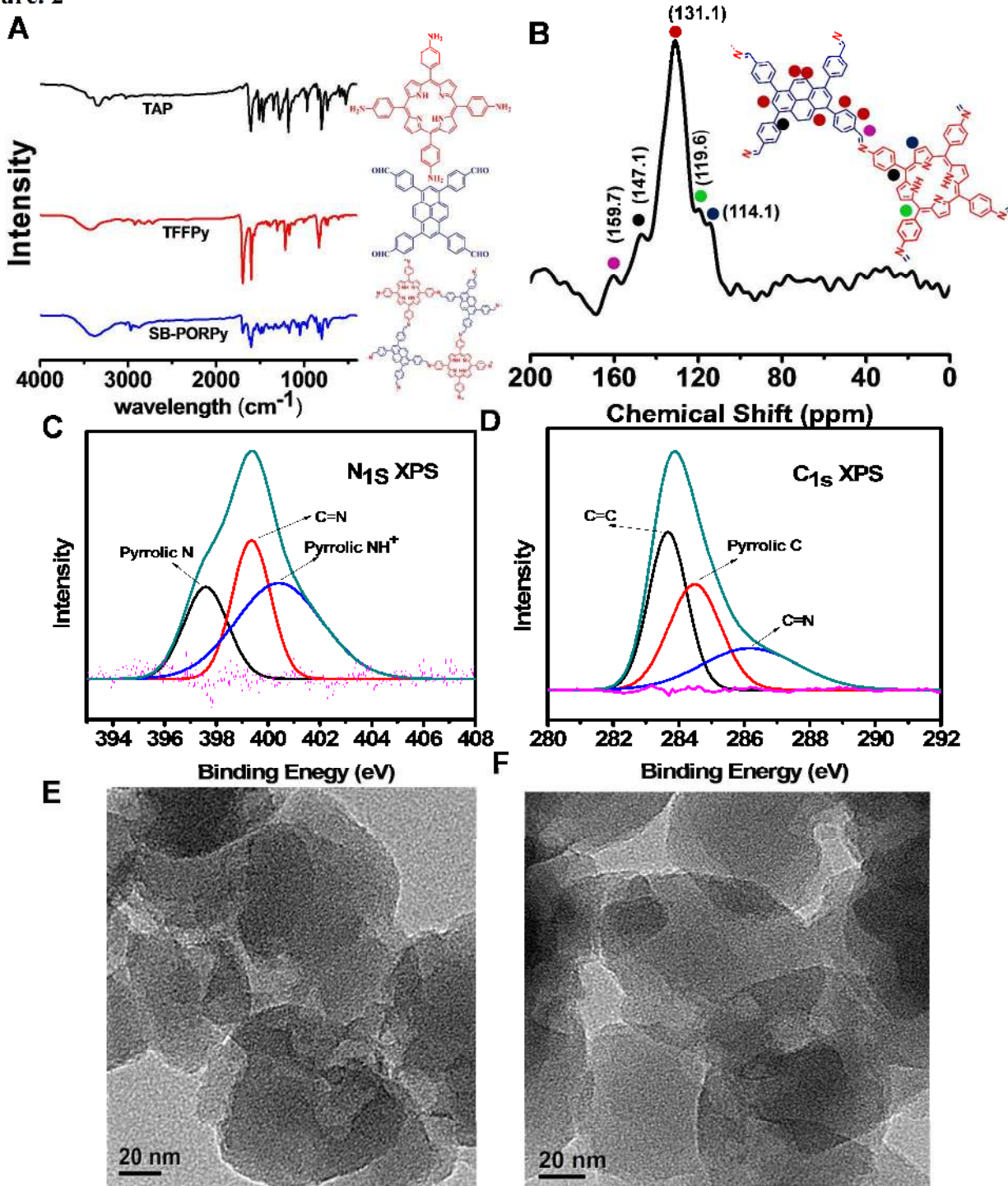


Figure 2. (A) IR spectra of SB-PORPy COF. (B) ^{13}C solid state CP-MAS NMR of SB-PORPy-COF; (C) N_{1s} peak SB-PORPy-COF and (D) C_{1s} XPS peak. High resolution transmission electron microscopy of SB-PORPy-COF at different region (E, F).

Figure. 3

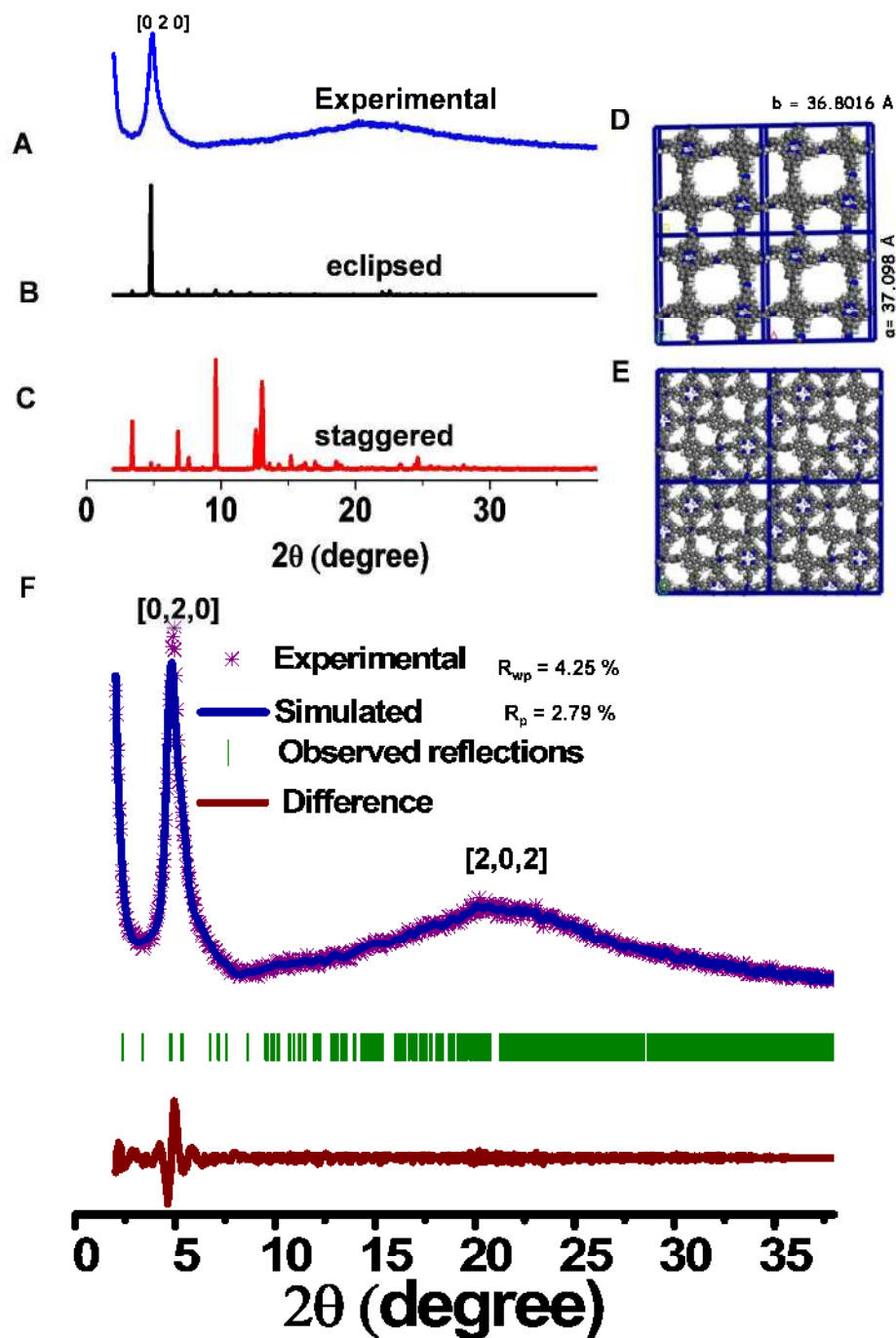


Figure 3. (A) Experimental PXR D (blue), (B) Theoretical AA (eclipsed) stacking (black), (C) Theoretical AB (staggered) stacking (red); (D) top view of simulated AA stacking and AB stacking (E) and Pawley refinement of PXR D (F).

Figure. 4

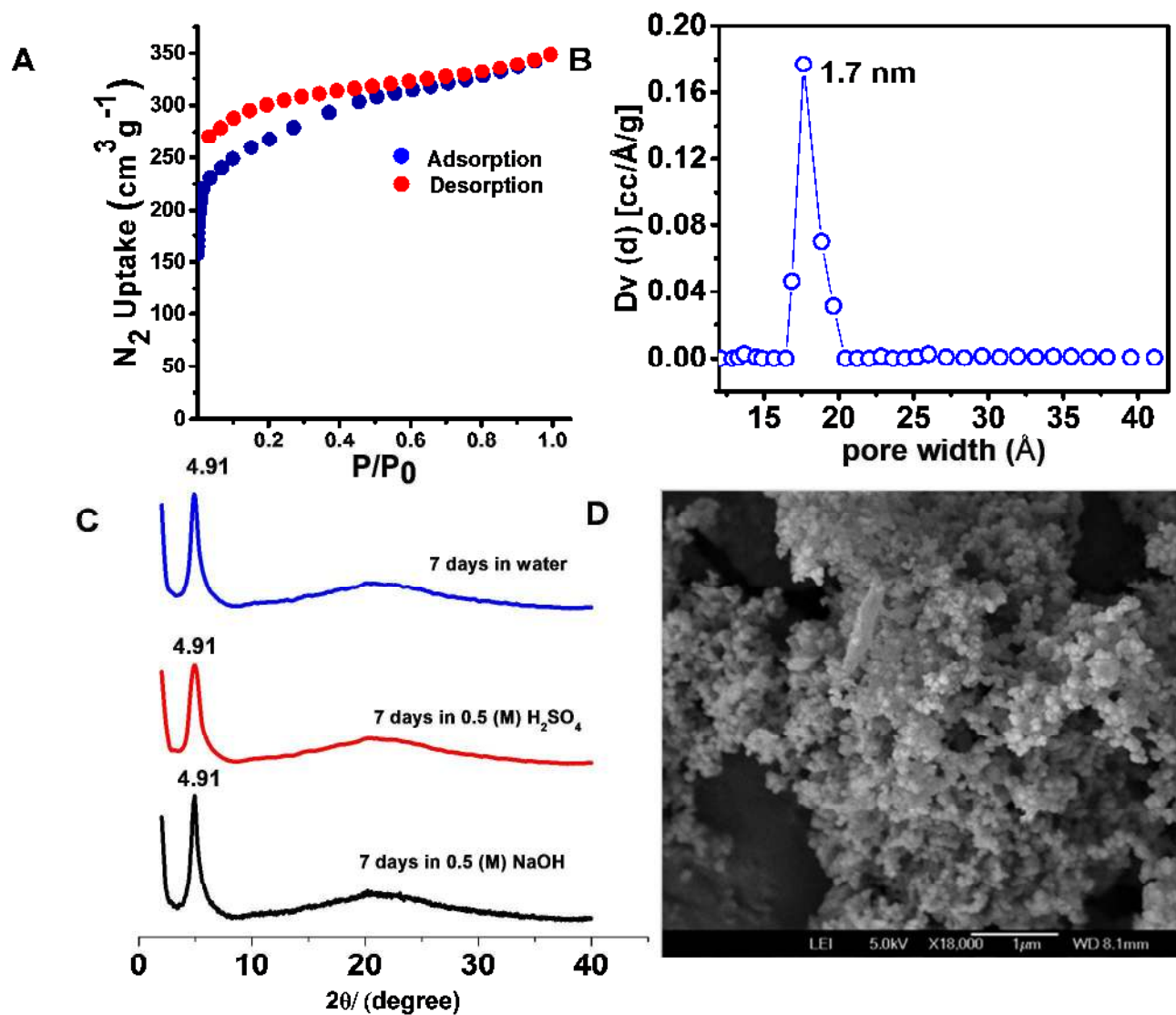


Figure 4. (A) N_2 adsorption (blue solid circle) /desorption (red solid circle) isotherm at 77K. (B) pore size distribution (blue empty circle). (C) Stability of SB-PORPy-COF in aqueous, acedic and alkaline media. (D) SEM image of SB-PORPy-COF

Figure. 5

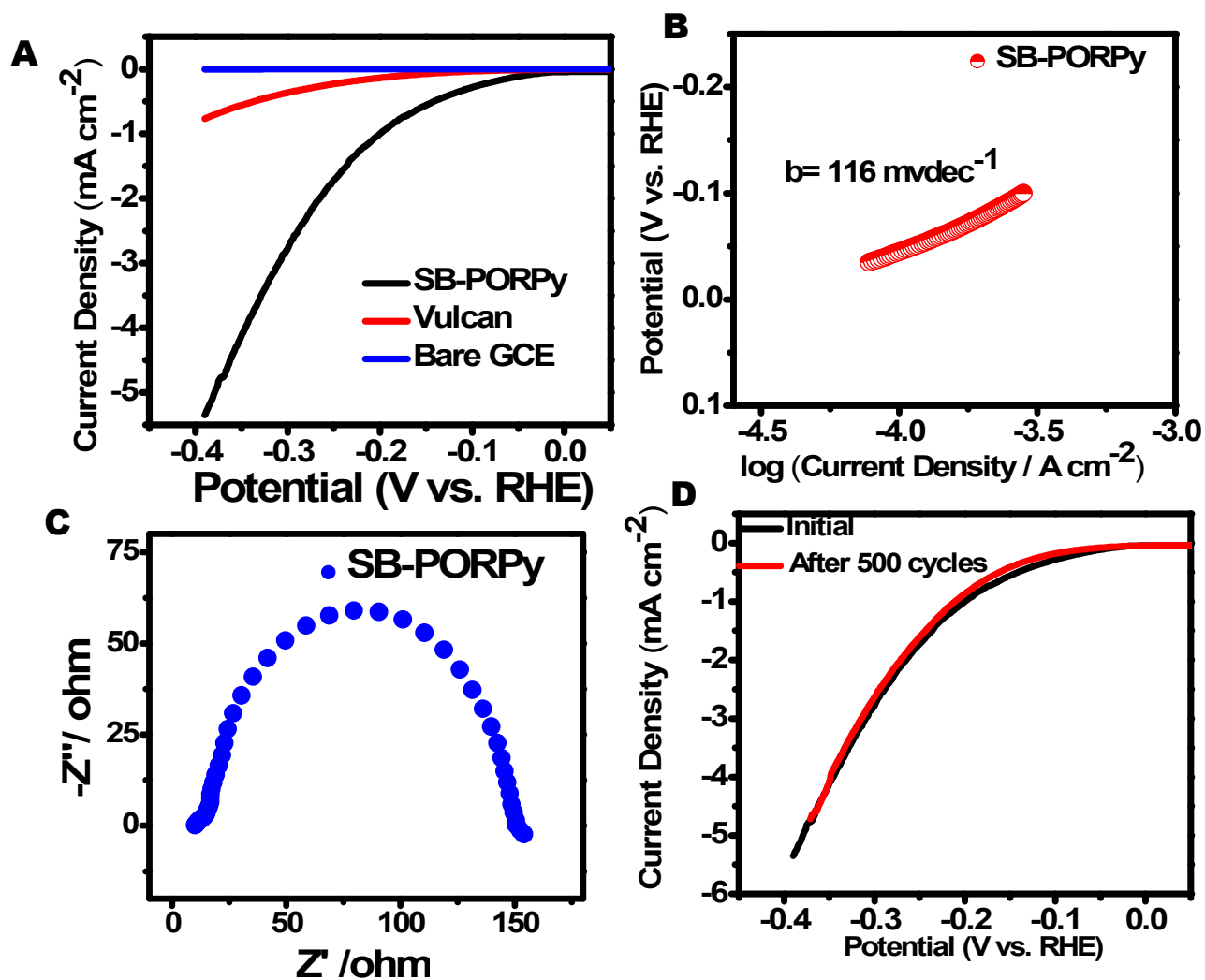


Figure 5. (A) Polarization curves for the hydrogen evolution reaction on bare GC (blue), Vulcan (red) and SB-PORPy-COF (black) electrodes. (B) Corresponding Tafel plot of SB-PORPy-COF electrode. (C) Impedance spectra (Nyquist Plot) of SB-PORPy-COF catalyst. (D) Linear sweep voltammograms of SB-PORPy-COF catalysts.

Figure. 6

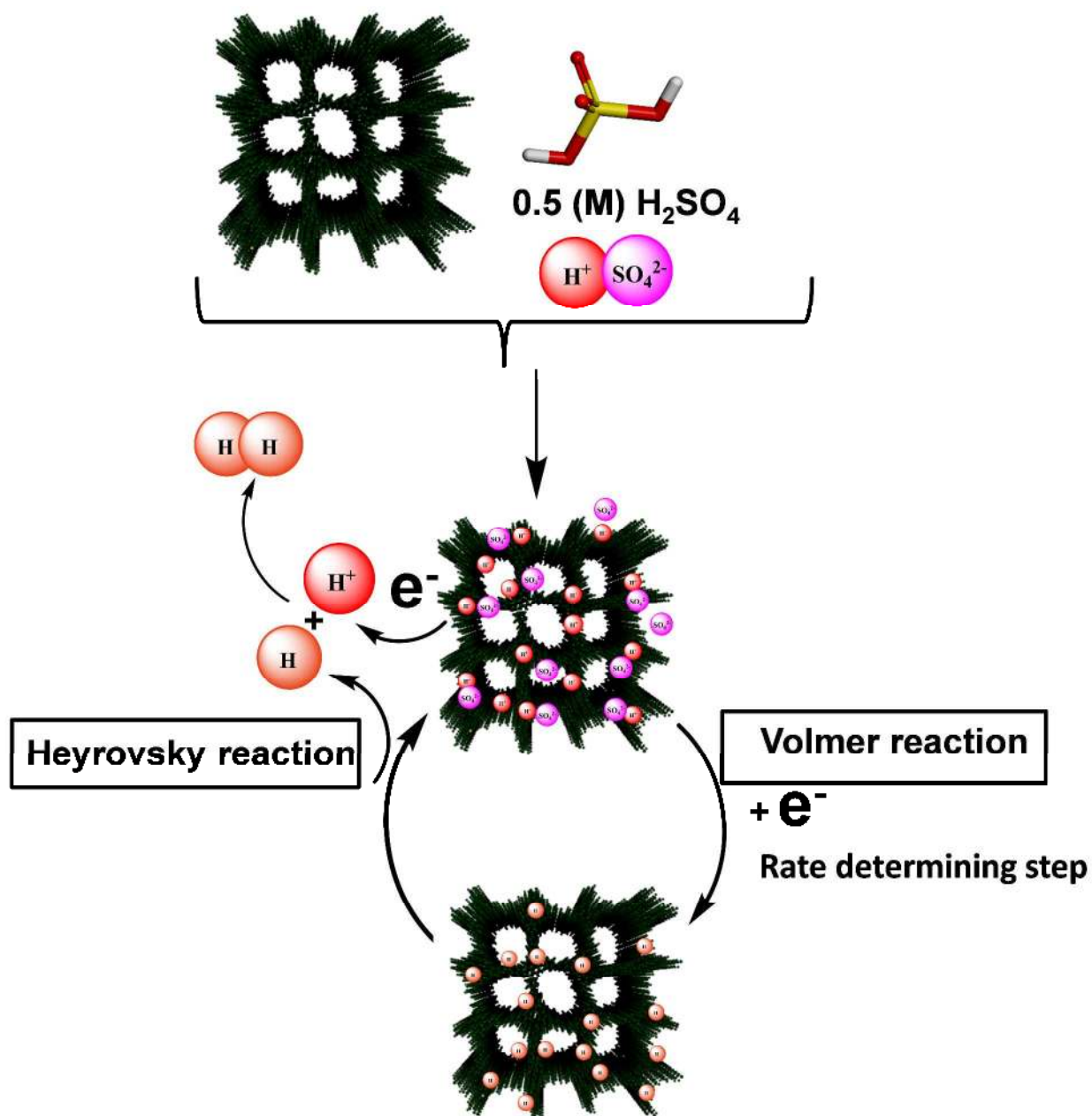


Figure 6. Possible volmar-heyrovsky pathway of hydrogen evolution reaction on SB-PORPy-COF

Electrochemical Stimuli Driven Facile Metal Free Hydrogen Evolution from Pyrene-Porphyrin Based Crystalline Covalent Organic Framework.

Subhajit Bhunia,^{†,||} Sabuj Kanti Das,^{‡,||} Rajkumar Jana,[§] Sebastian C Peter,[§] Santanu Bhattacharya,^{*,†} Matthew Addicoat,^{*,‡} Asim Bhaumik,^{*,‡} and Anirban Pradhan^{*,†}

