A New Azodioxy Linked Porphyrin Based Semi-conductive 2D Covalent-Organic Framework With I_2 Doping Enhanced Photoconductivity

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General Information

All the reactions except the COF synthesis step are performed under dry Ar- atmosphere with rigid exclusion of the moister using schlenk line.THF and toluene was dried over sodium metal under nitrogen atmosphere. The flash chromatographies are performed using 200-300 mesh silica. The progresses of the reactions were monitored by thin layer chromatography.

The FT-IR spectra were recorded on a Bruker VERTEX70 FT-IR spectrometer in 4000-400 cm^{-1} region using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. Thermogravimetric analyses were done on a NETZSCHSTA449C analyzer with a heating rate of 10 ˚C per minute, with a N_2 flow rate of 20 mL min^{-1}. UV-Vis-IR spectra of the compounds were recorded on a Perkin-Elmer Lambda 900 UV-Vis spectrophotometer. The samples were ground into fine powder and pressed onto a thin glass slide holder where $BaSO_4$ plate was used as a standard (100% reflectance). The field emission scanning electron microscopy (FE-SEM) of the materials was performed on a JEOL model JSM-6700 FE-SEM operating at an accelerating voltage of 1.5 or 5.0 kV. TEM image was obtained on a JEOL- 2010 transmission electron microscope at an acceleration voltage of 200 kV. The powder X-ray pattern of the powdered sample was recorded on a Rigaku MiniFlex 600diffractometer using Cu $K_\alpha$radiationby keeping the powdered sample on a silicon substrate, from 2.5 to 50˚. Nitrogen sorption isotherms were measured at 77 K with a Bel Japan Inc. model BELSORP-mini II analyzer. Before measurement, the samples were degassed in vacuum at 150 °C for overnight. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using density functional theory (DFT) model, the pore volume was derived from the sorption curve.

The electrical measurements of POR-COF and I_2 doped POR-COF were performed in air at room temperature using a Keithley 4200. For this purpose, pallets of POR-COF and I_2 doped POR-COF were prepared by mixing with 20 wt% of PMMA, where the both faces of the pallets were painted with silver paint. The pallets were dried in air for few hours in air before the electrical measurements. For photoconductivity measurement the sample was prepared by sandwiching a thin film of the samples between ITO glasses. The thin films were prepared by drop-casting an acetone suspension of the samples on ITO glasses.

Synthetic Procedures:

Tetrabromoporphyrin was prepared by a reported procedure.[1]

Synthesis of 2-(Trimethylsilyl) ethyl N-hydroxycarbamate (TeocNHOH):
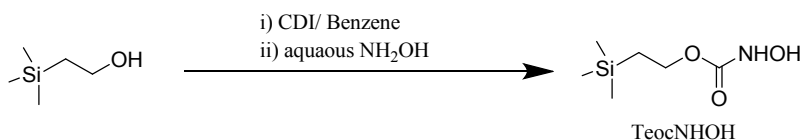
2-(trimethylsilyl) ethanol (8.95 mL, 62.5 mmol) was added to a suspension of 1, 1'-carbonyldiimidazole (11.15 g, 69 mmol) in distilled benzene (70 mL) and the resulting mixture was stirred at room temperature for about 5 hours to yield a colorless precipitate. To that colorless precipitate aqueous hydroxylamine (5.0 M, 22.5 mL, 110 mmol) was added and the resulting mixture was stirred another for 12 h. After that, the organic layer was separated using a separating funneland the aqueous part was washed with ethyl acetate (2× 50). The combined organic extracts were dried over sodium sulfate and the solvent was removed under reduced pressure to give colorless oily product. Finally, the colorless solids of the pure compound were obtained by flash chromatography using 40: 60 mixtures of ethylacetate and hexane as eluent. Percentage yield 80%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.13 (bs, 1H), 6.49 (bs, 1H), 4.28-4.24 (t, J= 8.8, 2H), 1.04-1.00 (t, J=, 2H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 159.1, 64.4, 17.6, -1.4; FT-IR (wavenumber, cm^{-1}) 3266, 2945, 2908, 1675, 1518, 1475, 1269, 1255, 1126, 1059, 930, 858, 832.

Synthesis of 2-(Trimethylsilyl) ethyl N-(tert-butyldimethylsilyloxy) carbamate (TeocNHOTBS):
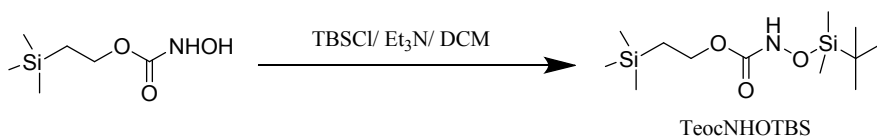

TeocNHOH (8.85 g, 50 mmol) was dissolved in dichloromethane (100 mL) and triethylamine (8.0 mL, 57.5 mmol) was added to it at 0°C. Then, a solution of tert-butylchlorodimethylsilane (7.9 g, 52.5 mmol) in dichloromethane (50 mL) was added drop wise to the above mixture. The mixture was allowed to warm to room temperature and allowed to stir for overnight. Water (100 mL) was added and the phases were

separated using a separating funnel.The organic layer was collected and then washed with water ($2\times$ 50 mL), dried over sodium sulfate, and filtered. The solvents were removed under reduced pressure to give an oily residue. Finally, and flash chromatography using 10:90 mixture of EtOAc: hexanes afforded the title compound as a colorless solid. Percentage yield: > 90%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 6.80 (bs, 1H), 4.27-4.23 (t, J= 8.8, 2H), 1.06-1.02 (m, 2H), 0.97 (s, 9H), 0.19 (s, 6H), 0.06 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 159.1, 64.4, 25.8, 18.0, 17.6, -1.5, -5.7; FTIR (wavenumber, cm^{-1}): 3270, 2949, 2923, 2892, 2855, 1721, 1690, 1342, 1250, 1100, 831.

Synthesis of protected tetrakis(hydroxylamine)porphyrin (1):
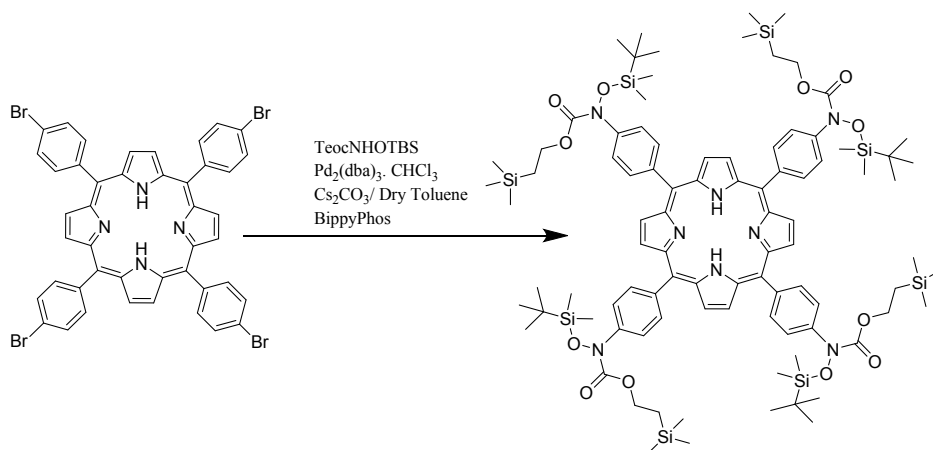
A mixture of tetrabromoporphyrin (2.32 g, 2.5 mmol), TeocNHOTBS (3.20 g, 11 mmol),Pd$_2$(dba)$_3$.CHCl$_3$ (130 mg, 0.125mmol), BippyPhos (254 mg, 0.5 mmol), and Cs$_2$CO$_3$ (6.5 g, 400 mmol) in toluene was sparged with dry N$_2$ for about 20 minutes. The resulting purple mixture was stirred at 110 °C for 30 hours. Dichloromethane (100 ml) was added to the reaction mixture and the solution was passed through a 5cm celite column. The solvent was removed under reduced pressure to give the brick-red colored crude product. Finally the desired product was obtained by the purification of the crude product using column chromatography where 5: 95 ==mixtures== of ethylacetate/ hexane was used as eluent.Percentage yield: >70%. ^{1}H NMR (400 MHz, CDCl$_3$) δ:8.88 (s, 8H), 8.21-8.19 (d, J= 8Hz, 8H), 7.88-7.86 (d, J= 8Hz, 8H), 4.49-4.45 (t, J=8Hz, 8H), 1.27 (m, 8H), 1.13 (s, 36H), 0.34 (s, 24H), 0.14 (s, 36H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 156.6, 143.1, 139.3, 134.3, 120.6, 119.6, 65.4, 25.9, 18.27, 17.85, -1.4, -5.0; FTIR (wavenumber, cm^{-1}): 3453, 3320, 2955, 2930, 2896, 2859, 1737, 1716, 1502, 1471, 1384, 1317, 1292, 1248, 1180, 1090, 1006, 966, 935, 833, 784, 750, 694; LC-MS: 1771.8.
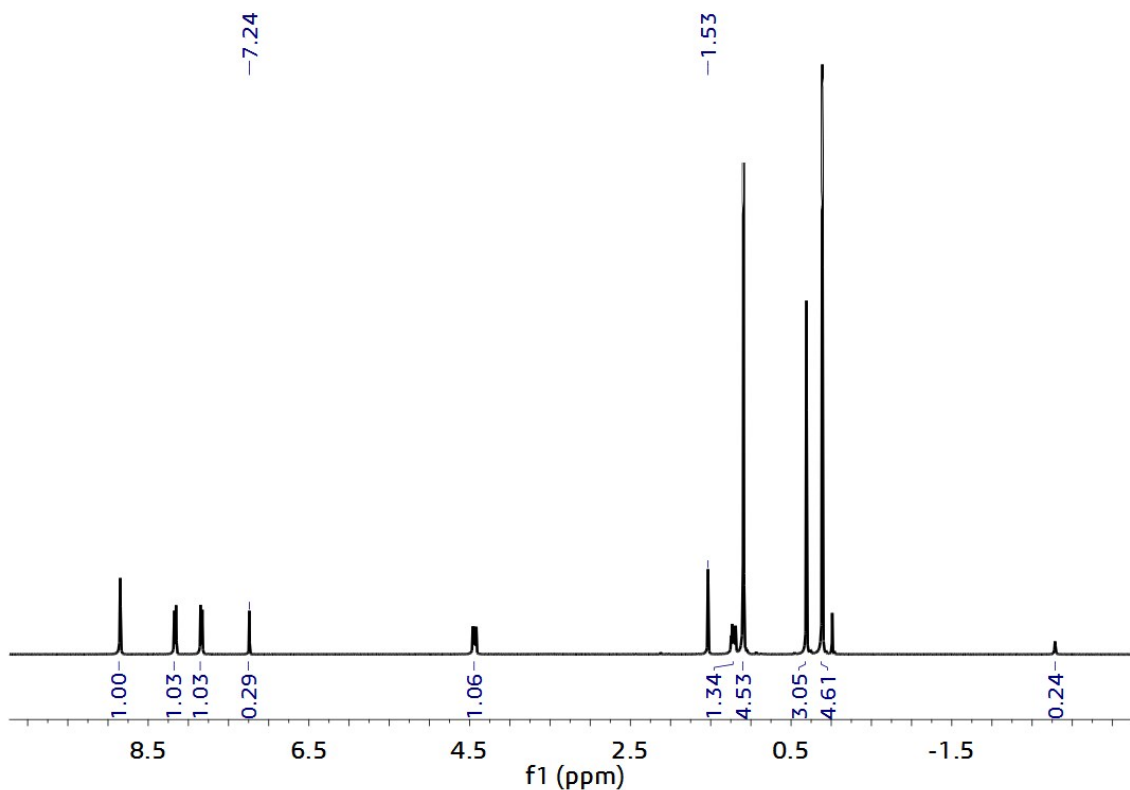
Figure S1 ^{1}H-NMR of the protected tetrakis(hydroxylamine)porphyrin**(1)**.

Synthesis of POR-COF:

442 mg of protected tetrakis(arylhydroxylamine)porphyrin (1) is dissolved in 20 ml of dry THF to which tetrabutylammonium fluoride (1.0 M in THF, 4 mL, 4 mmol) is added and the reaction mixture was allowed for continuous stirring at room temperature for 12 hours. The reasulting reaction mixture was treated with 5 ml (5 M) of aquaous ammonium chloride and stirred for another few minutes. The solid product was collected by filtration and washed with THF, chloroform and at last with methanol for several times until the filtrate become colorless to get purple colored POR-COF powder. The purple powder was degassed in vaccum oven at 150 ˚C for overnight for further analysis.Yield: 140 mg (79%); IR (cm^{-1}): 3429, 2961, 2921, 2841, 1603, 1460, 1341, 1280, 967, 855, 801, 728, and 710.

Preparation of I$_2$ doped POR-COF:

The inclusion of iodine was performed by immersing the activated POR-COF in a solution of iodine in n-hexane (2 mL, 0.1M/L) for 30 hours. The I$_2$ included POR-COF was obtained as black powder after filtration, which was washed many times with n-hexane until the filtrate become colorless. The I$_2$ doped POR-COF was dried in oven at 70 C ˚for overnight before the electrical measurements.

Structure Modeling

To build the crystal structure of POR-COF, the unit cell parameters and the atomic positions were generated using Material Studio 8.0 software package. According to the describable peaks in PXRD pattern, gas sorption analysis, IR, Raman as well as NMR spectra, a possible crystal structure model of POR-COF was simulated. The simulated structure has a $P4$ space groupwith $a= b= 39.0$ Å, $c= 3.5$ Å, and $\alpha= \beta= \gamma= 90°$. The PXRD pattern simulated from this modeled structure shows good agreement with the observed one.
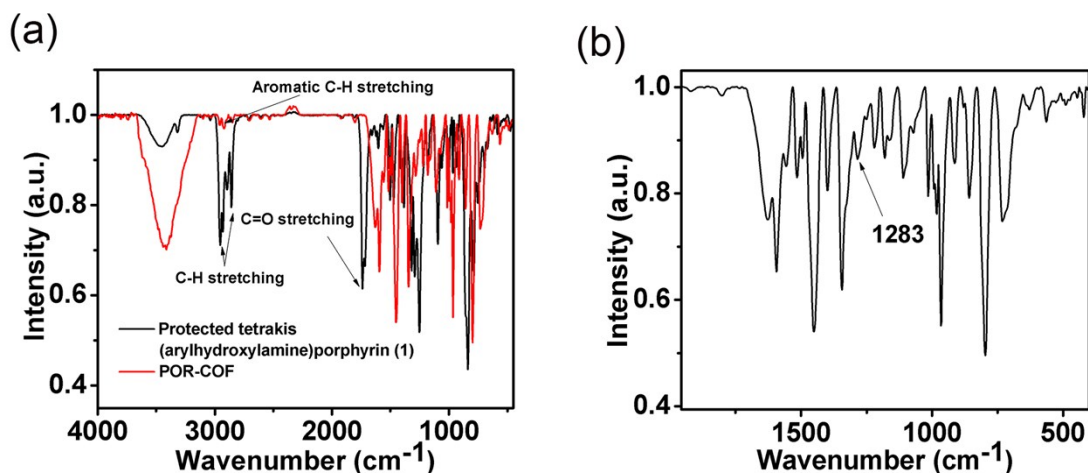
Figure S2 (a) Comparison of theft-IR spectra of POR-COF with the protected tetrakis(hydroxylamine) porphyrin; **(b)** Expanded FT-IR spectra of POR-COF for the 2000-450 cm⁻¹ region.
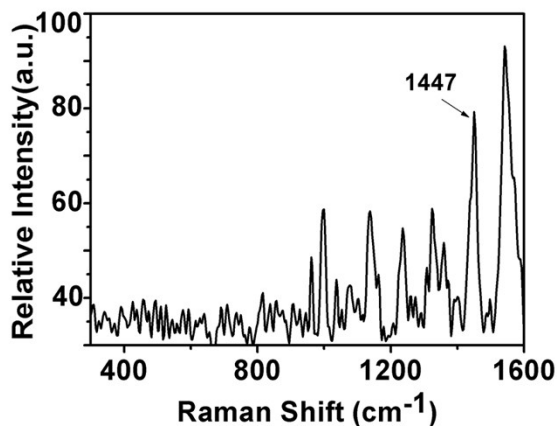

Figure S3 Raman spectra of POR-COF.

Table S1 Assignment of the IR peaks:

| Peak (cm^{-1})	Assignments and notes
3420	N-H stretching of the pyrrole rings
2961, 2921, 2841	C-H stretching of the phenyl rings
1603	C=C stretching of the pyrrole rings
1460	C=C vibrational mode of the phenyl rings
1341	Pyrrole deformation
1283	Trans nitroso dimers (trans-azodioxy)
967, 855	C-N stretching
801	C-H out-of plan bending of the phenyl ring
728,710	C-H (trans) out of plan bending of the phenyl rings
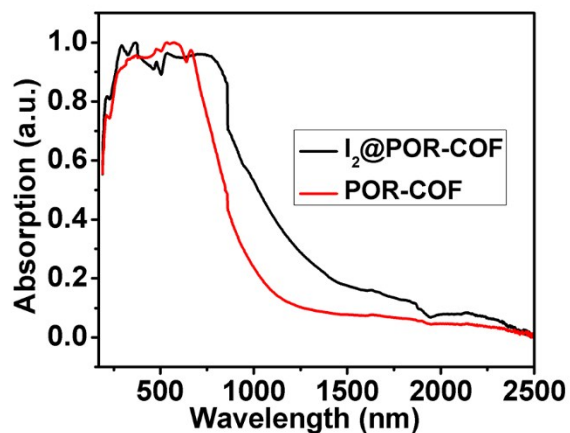
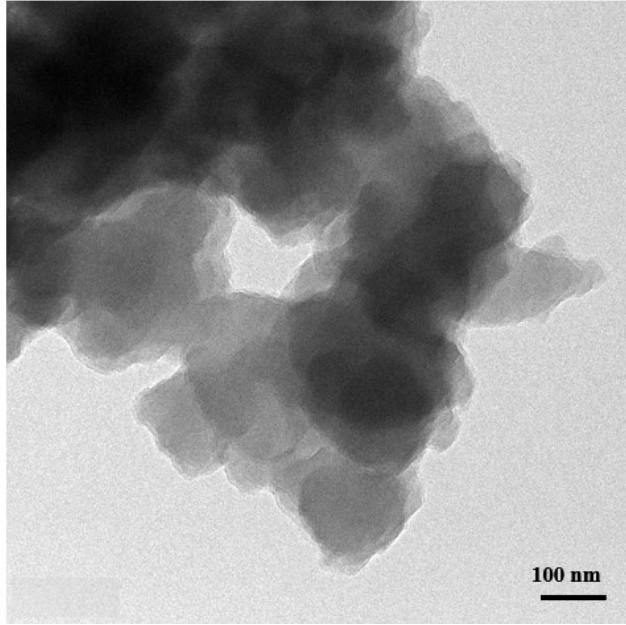**Figure S4** The electronic spectra of POR-COF and I$_2$ doped POR-COF.
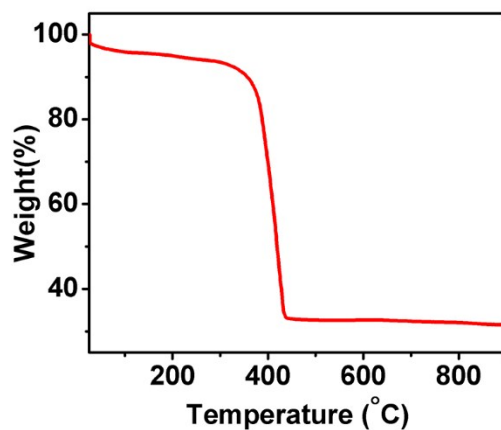
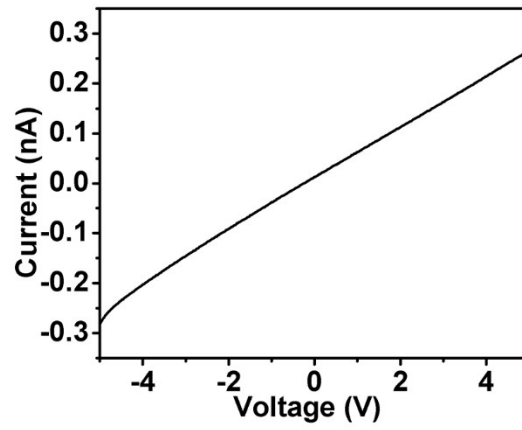**Figure S5** TG of POR COF and I$_2$ doped POR-COF.
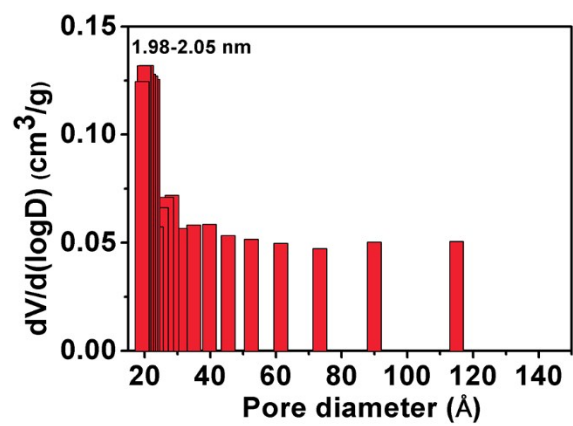
Figure S6 Pore-size distribution of POR-COF using BJH method.
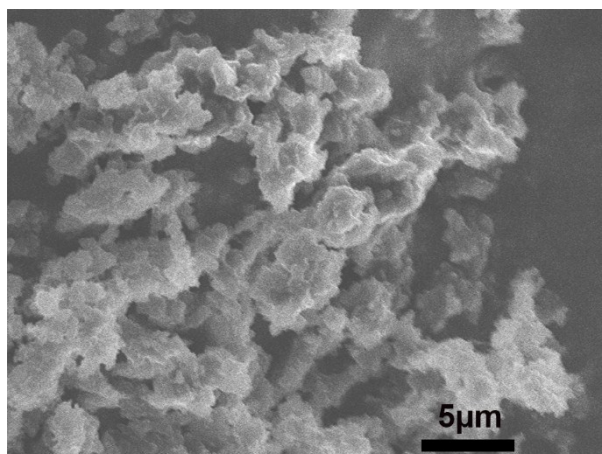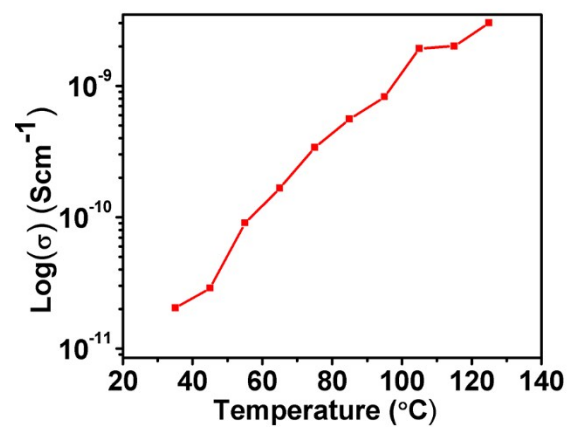

Figure S7 SEM image of POR-COF.

Figure S8 TEM image of POR-COF.

Figure S9 I-V profile of POR-COF with 20 wt% of PMMA at room temperature in air.

Figure S10 Temperature dependent conductivity of POR-COF.

References:

1. L. Chen, Y. Yang, D. Jiang, *J. Am. Chem. Soc.*, 2010, **132**, 9138-9143.