Supporting information

The Potential of a Graphene-Supported Porous-Organic Polymer (POP) for CO_2 Electrocatalytic Reduction

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Experimental

All reagents were used as received without further purification. Solvents, catalysts, and common chemicals were purchased from Sigma-Aldrich or Fisher Scientific-UK. Brominated aromatics were purchased from Combi-Blocks. Triethynylbenzene was synthesized as described below. Nitrogen and CO_2 gases for sorption were purchased from Airliquide (N_2 AlphaGaz2 (99.999%) and CO_2 (99.995%)), Graphene (Alfa Aesar, catalogue 47312), copper(I) iodide (CuI, 98%, Acros Organics); triethylamine (Chromanorm®, HPLC grade, VWR); Acetonitrile (fischer, analytical reagent grade 99.99%).

Gas sorption analysis was performed on Micromeretics **ASAP2020** and the variable temperature CO_2 isotherms were recorded in insulated dewar connected to **LAUDA RA-8** circulating chiller. The apparent surface areas were determined from the nitrogen adsorption isotherms collected at 77 K by applying the Brunauer-Emmett-Teller (BET) and Langmuir models. Pore size analyses were performed using a slit NLDFT pore model system by assuming a carbon finite pores surface. The determination of the isosteric heats of adsorption (Q_{st}) for CO_2 was estimated by applying the Clausius-Clapeyron expression using the sorption isotherms measured at variable temperatures. CHN elemental analyses were conducted on ThermoScientific **Flash 2000**. Infra-red absorption spectra were recorded on ThermoScientific **Nicolet is-10**. Thermogravimetric analyses were conducted on Thermal Analysis-**Q50** under nitrogen atmosphere. TEM images were acquired on a JEOL JEM-2100, operating at 200 KV.

Solid-state NMR: Solid-state ^{13}C CP-MAS spectra were collected on a Bruker Avance III-HD 500 MHz spectrometer fitted with a 1.9 mm MAS probe. The spectra were collected at ambient temperature with sample rotation rate of 20.0 kHz. Cross polarization was performed with a 2.0 ms contact time with linear ramping on the ^{1}H channel and 62.5 kHz field on the ^{13}C channel. 1H dipolar decoupling was performed with SPINAL64 modulation and a 147 kHz field strength. Free induction decays were collected with a 22 ms acquisition time over a 300 ppm spectra width with a relaxation delay of 2.0 s.

Synthesis of 1,3,5-triethynylbenzene.

In a 100 mL pressure vessel, a mixture of THF (15 mL) and Et_3N (3 mL) was added, cooled in liquid nitrogen bath, degassed through three freeze-pump-thaw cycles and maintained under nitrogen atmosphere. To this prepared solution was added 1,3,5-tribromobenzene (3 mmol), ethynyltrimethylsilane (12 mmol, 1.22 g), CuI (10 mg, 0.05 mmol), PPh_3 (26 mg, 0.1 mmol) and $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol). The reaction mixture was then placed in an oil bath maintained at 80°C for 24 hrs. The solution was then filtered through fritted funnel and the volatiles removed under reduced pressure. The crude product was then purified through flash chromatography on silica gel using hexane (1%EtOAc) to isolate white crystalline solid (777 mg, 70% yield). The trimethylsilyl group was removed by dissolving the above product in THF (10 mL) and MeOH (10 mL) followed by addition of $K_2(CO_3)$ (1.8 g, 13 mmol) and stirring at room temperature overnight. The reaction was quenched by addition of HCl (1M) and the product extracted in DCM, then dried over $Mg(SO_4)$, filtered and the volatiles were removed under reduced pressure to yield the 1,3,5-triethynylbenzene in 222mg, 1.48 mmol, 70% yield. ^1H NMR (CHLOROFORM-d ,300MHz): d = 7.59 (s, 3 H), 3.13 ppm (s, 3 H)

Synthesis of PyPOP@Graphene:

In a 100 mL pressure vessel, a mixture of DMF (15 mL) and Et3N (2 mL) was added, cooled in liquid nitrogen bath, degassed through three freeze-pump-thaw cycles and maintained under nitrogen atmosphere. To this prepared solution was added graphene powder (8 mg), 4,6-dibromopyrimidine (23 mg, 0.1 mmol), 1,3,5-triethynylbenzene (15 mg, 0.1mmol), and the tube was sonicated for 30 minutes, then was added CuI (5 mg, 0.026 mmol), PPh3 (5 mg, 0.019 mmol) and PdCl2(PPh3)2 (5 mg, 0.014 mmol), then sealed with a Teflon screw under flow of nitrogen. The reaction mixture was then placed in an oil bath maintained at 80°C for 24 hours. A dark olive-black solid was formed which was filtered under vacuum through a sintered glass funnel, washed with acetonitrile (CAN) and left to exchange in ACN at 60°C in sealed vial under autogenous pressure for 6 hr, then filtered under vacuum and left to dry at 110°C for a few minutes before conducting further analyses. The total dry weight of the solid was 30 mg, quantitative yield based on the sum of the masses for starting material excluding the mass of Br atoms.

Synthesis of PyPOP

An identical synthesis was conducted for the PyPOP@G except for adding the graphene, as reported earlier.[1]

Electrochemical measurements:

In a typical run, 5 mg of the studied solid (PyPOP@G or G) was mixed with 15 mg of carbon paste and grinded in agate mortar to ensure homogenous distribution inside the carbon paste. This prepared material was then packed inside a carbon paste electrode (CPE) of 3 mm cross section. The electrochemical measurements were conducted on a biologic SP-50 potentiostat/galvanostat in a three electrodes configuration. The working electrode was a CPE packed with the prepared slurry, Pt wire as a counter electrode and Ag|AgCl as a reference electrode. The electrolyte was aqueous $KHCO_3$ (0.1 M) degassed through bubbling of N_2 for 30 minutes (99.9999%, alphagaz2, AirLiquide), and saturated with CO_2 (99.995, AirLiquide), through bubbling for 30 minutes prior to measurements, the CO_2 flow was also maintained above the solution to ensure maintained CO_2 environment. CO_2 electrocatalytic reduction response was estimated using the linear sweep voltametry (LSV) technique. The working electrode potential was swept between 0V to -1.6 V with scan rate of 10 mV/s in 0.1M $KHCO_3$ as the electrolyte.

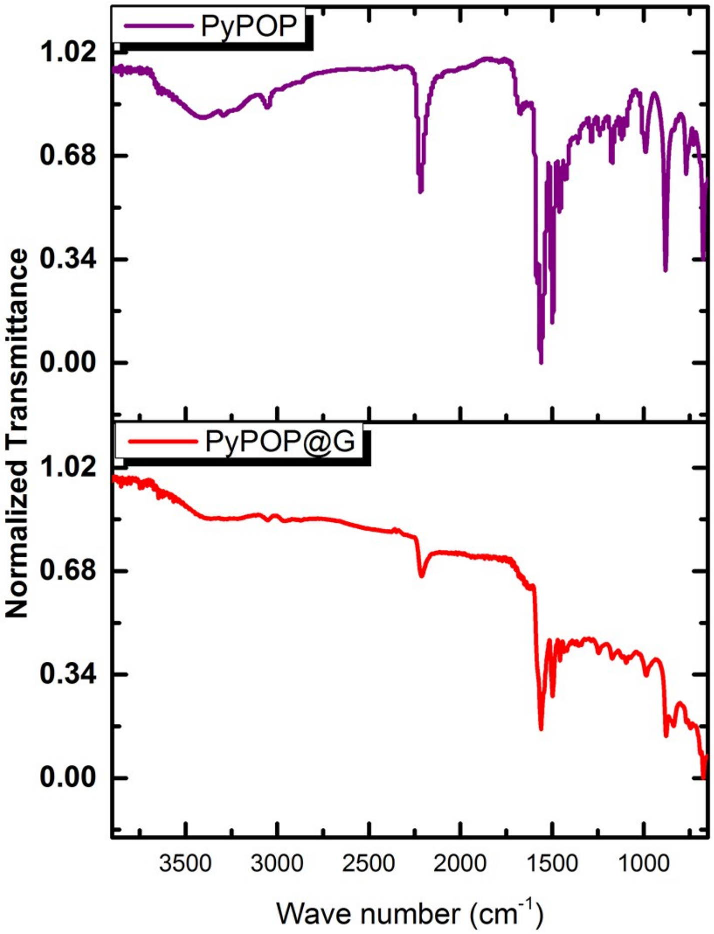


Figure S1. FTIR spectra for the PyPOP and PyPOP@G.

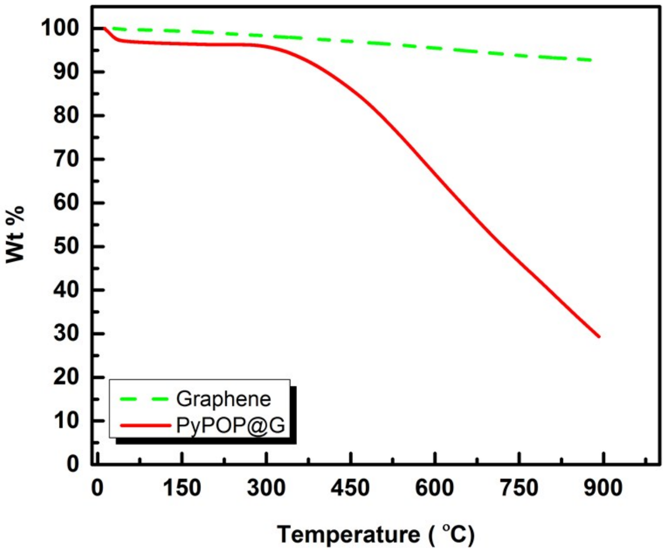


Figure S2. TGA analyses for the G and the PyPOP@G.

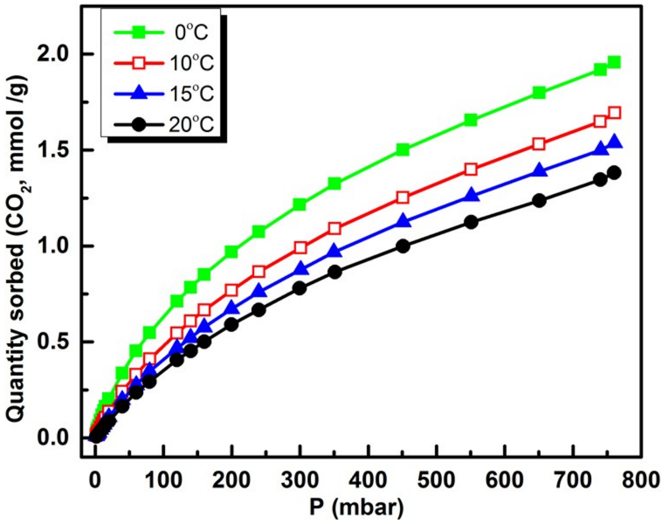


Figure S3. Variable temperature CO_2 sorption isotherms for the PyPOP@G.

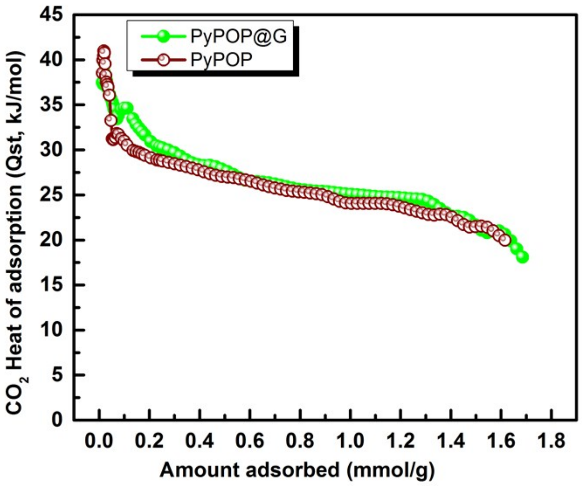


Figure S4. CO_2 (Qst) plots for the PyPOP and PyPOP@G.

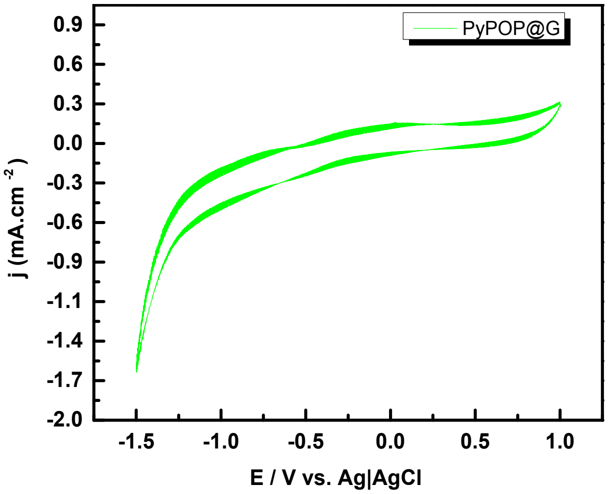


Figure S5. CV for the CPE electrode doped with PyPOP@G in 0.1M $KHCO_3$, CO_2 saturated solution.

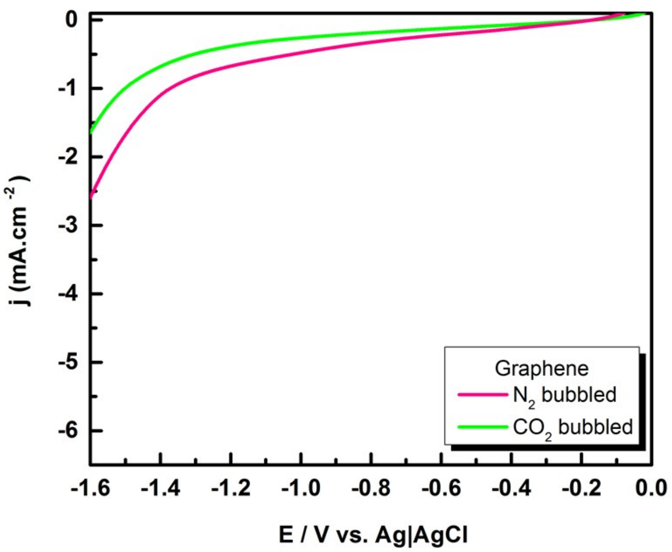
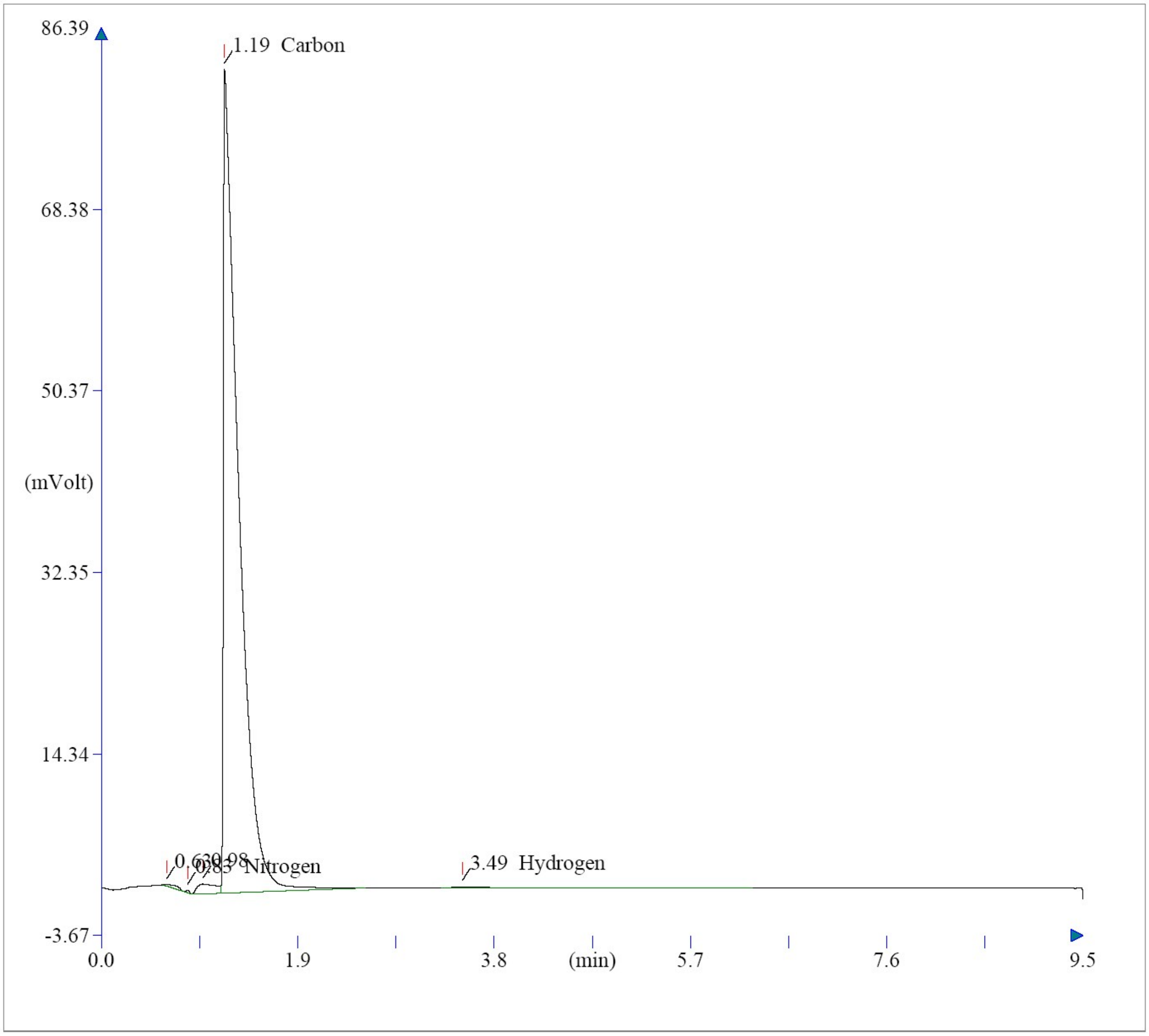


Figure S6. LSV for the electrode doped with graphene, 0.1M $KHCO_3$, N_2 saturated and CO_2 saturated solution.



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 Element Name                                 Ret.Time      Area     BC    Area ratio     K fac
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               1         0.0000        38       21557  RS                     0
Nitrogen                 0.0000        50        5042  RS   1641.313000  .17868
               3         0.0000        59      127121  FU                     0
Carbon                  94.3285        72     8274678  FU      1.000000  .48180
Hydrogen                 0.1393       210       43634  RS    189.640500  .15359
Totals                  94.4678               8472032
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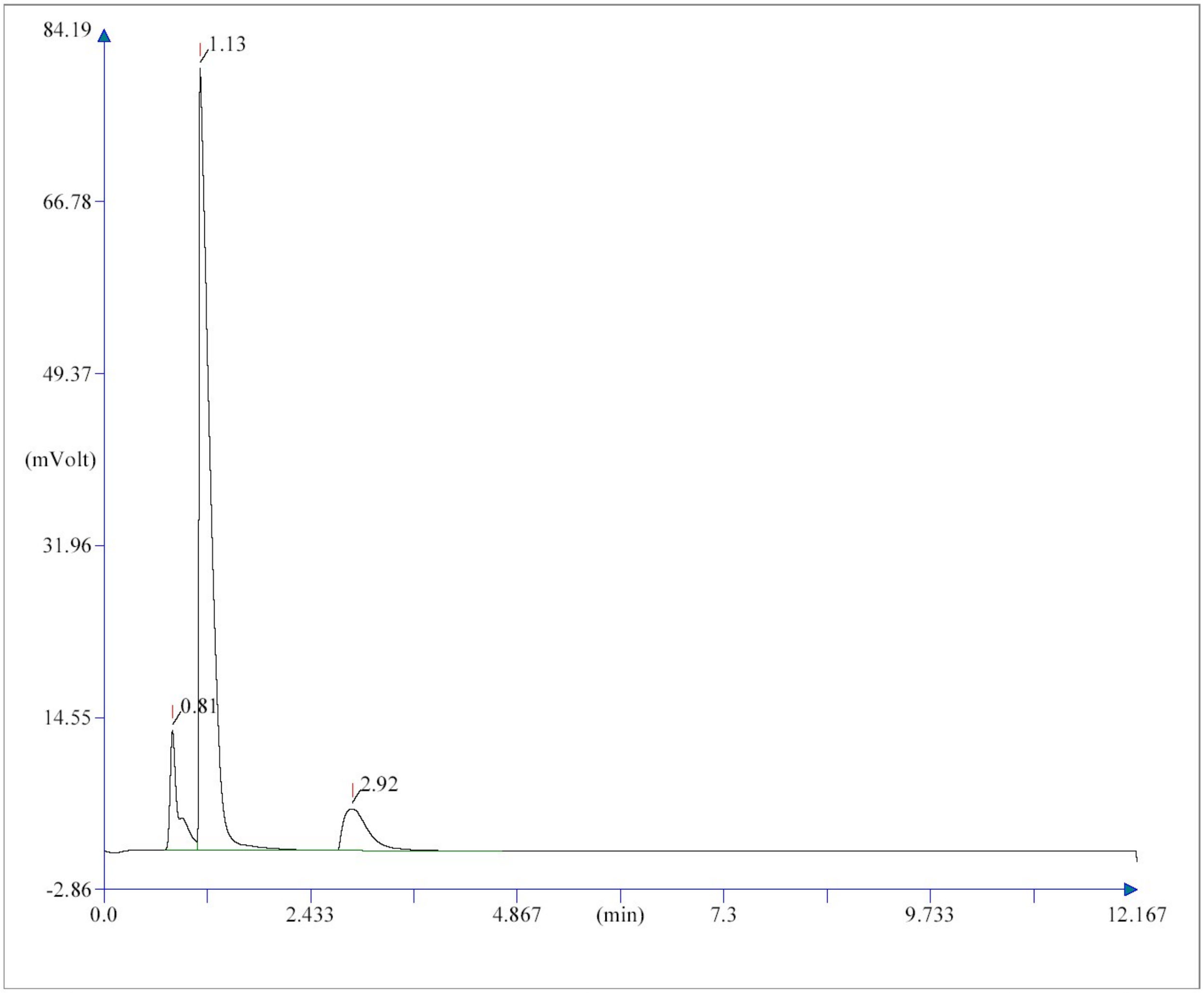
Figure S7. Elemental analysis for the graphene.



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  Element Name                       Ret.Time    Area     BC   Area ratio    K facto
---------------- ------------- -------- ---------- -- ------------ --------
Nitrogen                21.1428       49     823188 mi      8.412201  .189898E
Carbon                  71.5346       68    6924823 mi      1.000000  .470596E
Hydrogen                 2.6622      176     864404 mi      8.011095  .154992E
Totals                  95.3396             8612415
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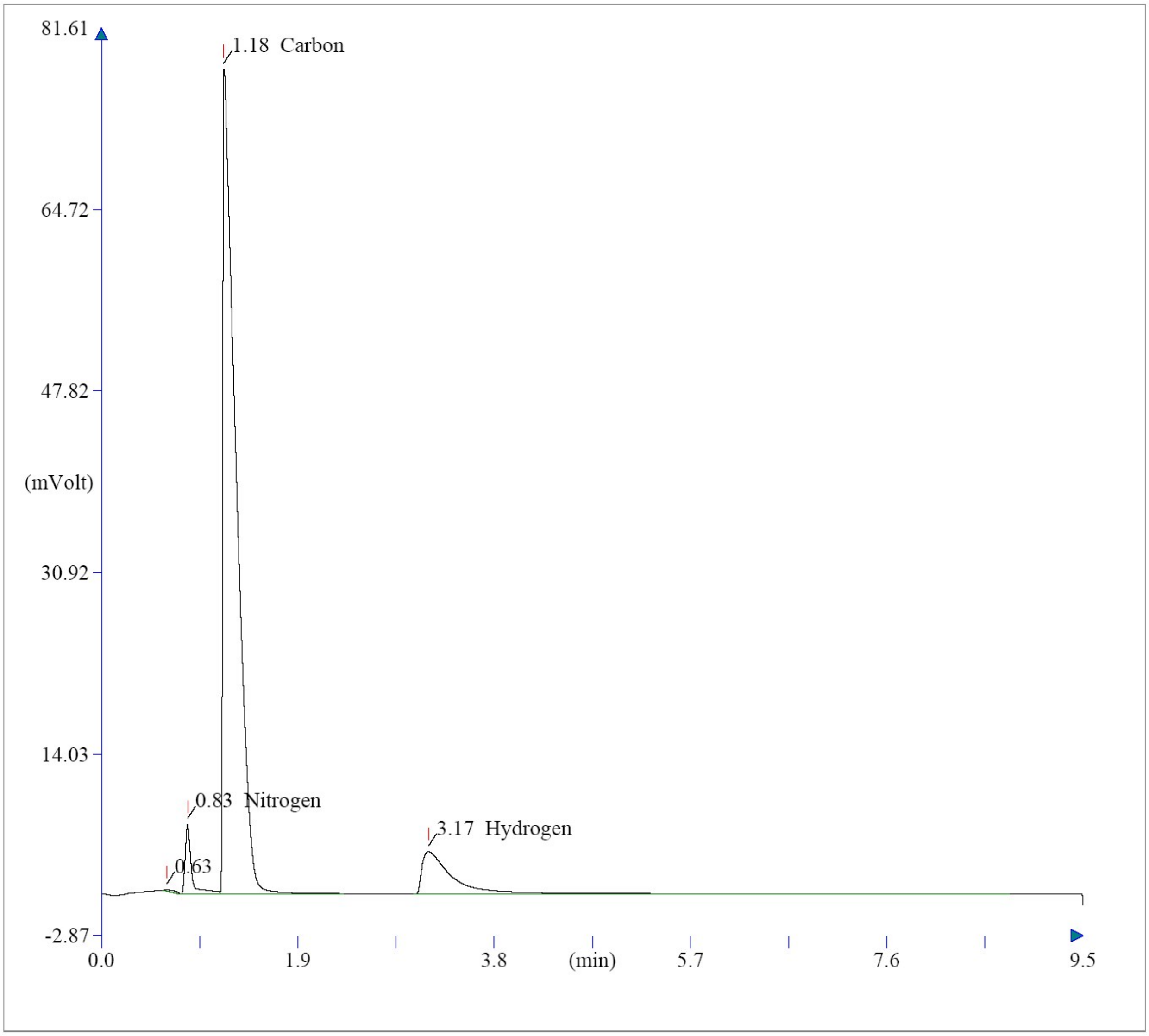
Figure S8. Elemental analysis for the PyPOP.



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  Element Name                          Ret.Time    Area     BC   Area ratio     K fac
--------------- -------------  --------  ----------  --  ------------  ------
        1                  0.0000        38       12492  RS                     0
Nitrogen                   6.6419        50      283320  FU     23.592920  .17868
Carbon                    76.4353        71     6684353  FU      1.000000  .48180
Hydrogen                   2.9597       190      819713  FU      8.154504  .15359
Totals                    86.0369               7799878
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Figure S9. Elemental analysis for the PyPOP@G.

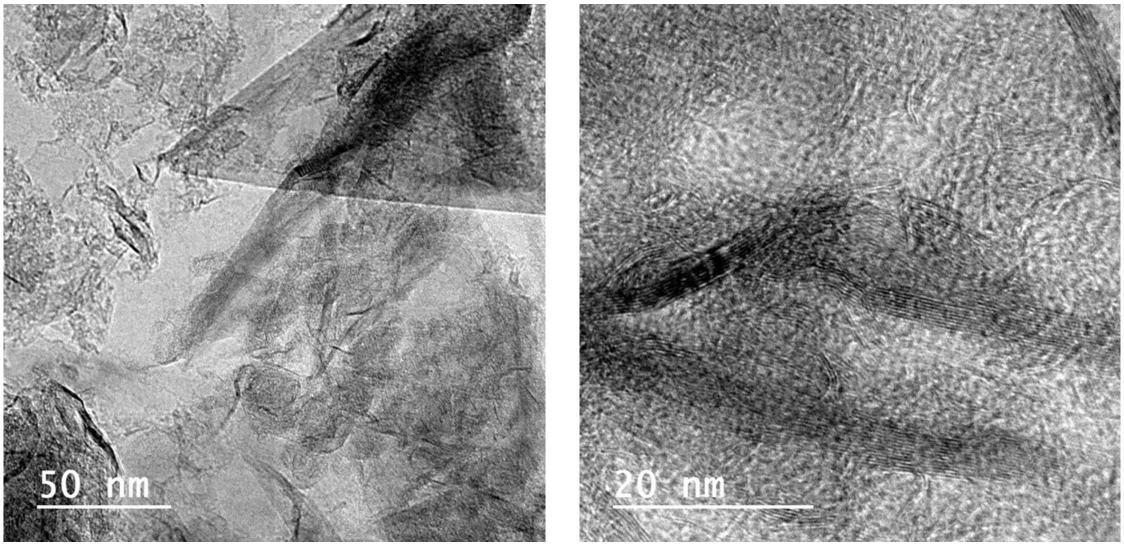


Figure S10. TEM images of the graphene support before deposition of the PyPOP, right image showing edges of graphene layers with some stacking.

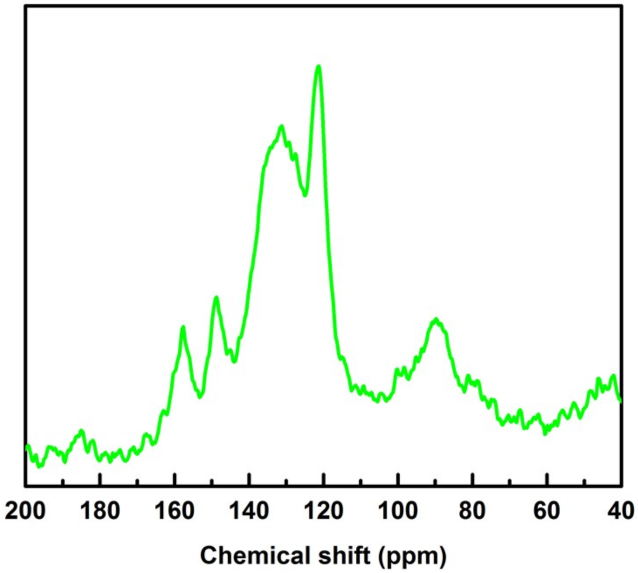
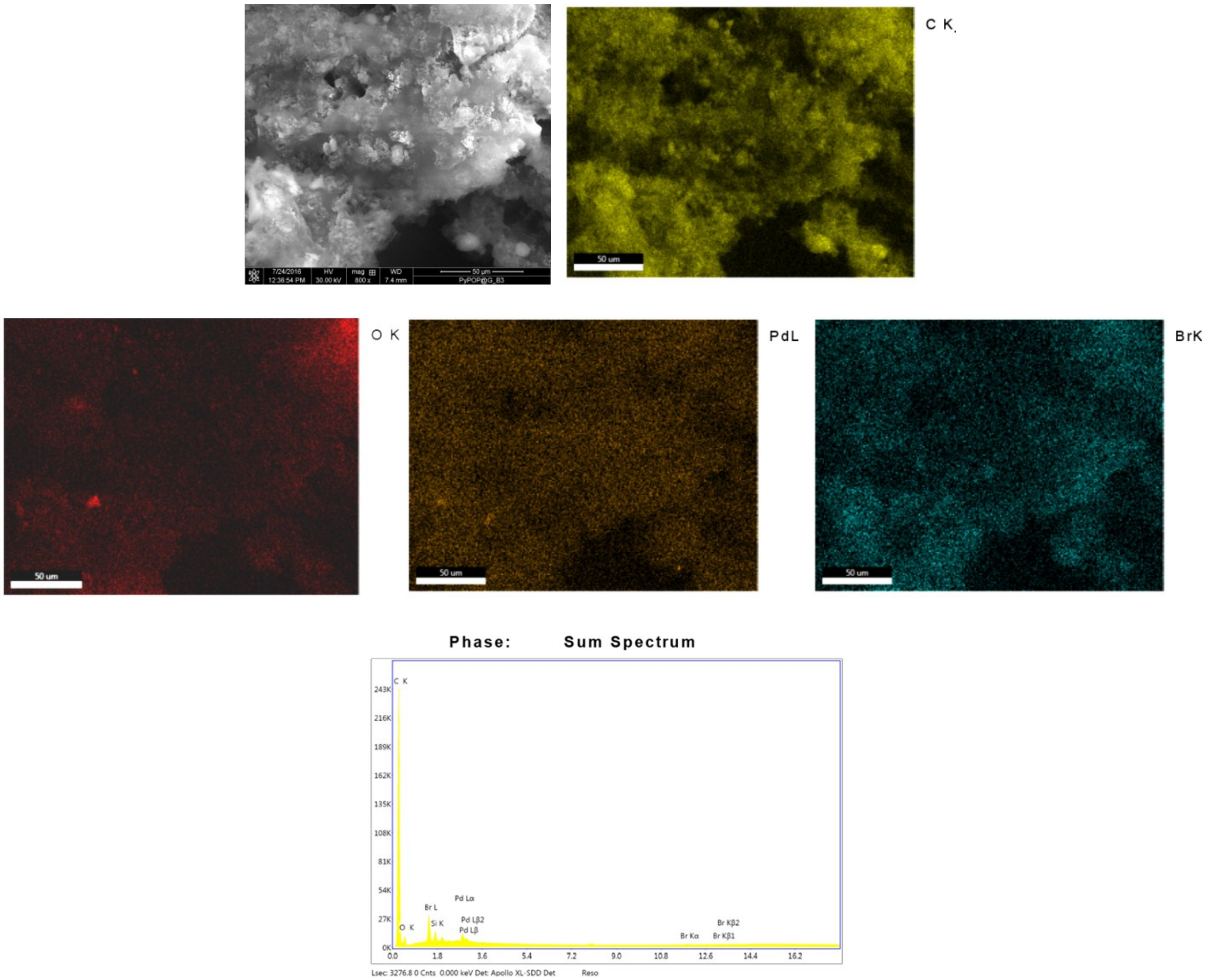


Figure S11. Solid-state, cross-polarization magic angle spin (CPMAS) NMR spectrum of the PyPOP@G, showing the PyPOP representative peaks for internal alkyne (90.5 ppm), aromatic carbons (benzene quaternary carbons and pyrimidine C-5 at ~120 ppm, and benzene C-H atoms at ~140 ppm), pyrimidine carbons (quaternary C-4,6 carbons at 148.8 ppm and α C-H carbon at 157.7 ppm).



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	84.79	88.77	630.5	0
O K	13.93	10.95	36.7	0
SiK	0.4	0.18	26.9	0
PdL	0.87	0.1	30.5	0.01
BrK	0.02	0	0.1	0.56

Figure S12. SEM image of the PyPOP@G (top left) and corresponding EDX mapping (labeled images), and (below) is the elemental analysis showing the major C composition of the material, some traces of Pd and Br from the synthesis, the oxygen detected is attributed to adsorbed moisture or oxygen from air trapped within the pores of the material.

Notes and References

1. Alkordi, M. H.; Haikal, R. R.; Hassan, Y. S.; Emwas, A.-H.; Belmabkhout, Y., Poly-functional porous-organic polymers to access functionality - CO2 sorption energetic relationships. *Journal of Materials Chemistry A* **2015,** *3* (45), 22584-22590.