

Electrochemically active porous organic polymers based on corannulene

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Supplementary Information

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1. Materials and methods

All reagents were purchased from commercial suppliers (Sigma-Aldrich and Fisher Scientific) and used as received. Low-pressure gas adsorption experiments (up to 760 torr) were carried out on a Micromeritics ASAP 2020 surface area analyzer. Ultrahigh purity grade N₂, CO₂ and H₂ were obtained from Airgas Corporation. Samples were degassed under dynamic vacuum for 12 h at 150 °C prior to each measurement. N₂, CO₂ and H₂ isotherms were measured using a liquid nitrogen bath (77 K) and CO₂ was measured in a room temperature water bath (298 K) and using an ice water bath (273 K). Pore size distributions were calculated from the adsorption curve using the nonlocal density function theory (NLDFT) carbon slit-pore model in the Micromeritics software package and heats of adsorption values were computed by the Micromeritics ASAP software package using a variant of the Clausius-Clapeyron equation. Fourier transform infrared (FT-IR) spectra were taken on a Nicolet 380 FT-IR with a Smart Orbit diamond attenuated total reflectance (ATR) cell. The thermogravimetric analyses (TGA) were performed using a TA Instrument SDT Q600 Analyzer under nitrogen atmosphere with a heating rate of 10 °C min⁻¹ from 30-800 °C. Powder X-ray diffraction (PXRD) of polymers was carried out on a Bruker D8 Advance diffractometer with a sealed tube radiation source (Cu K α , λ = 1.54184 Å), a no background sample holder, and a Lynxeye XE detector. Scanning electron microscope (SEM) images were acquired with Zeiss-LEO model 1530 SEM instrument and energy dispersive X-ray spectroscopy (EDX) were acquired on a Zeiss SUPRA40 SEM instrument. The samples were prepared on 15 mm aluminum stubs using double-sided adhesive copper tapes. For EDX uncoated samples were imaged at a working distance of 10 mm and a voltage of 15 kV using a secondary electron detector. Fluorescence measurements were carried out on a Perkin-Elmer LS-50B Luminescence Spectrophotometer with a suspension of BB-POPs (1 mg) in dichloromethane (3 mL). Cyclic voltammetry (CV) was performed using a Potentiostat/Galvanostat (EG&G Princeton Applied Research 273A) in an anhydrous DMF solution of Bu₄NPF₆ (0.1 M). Voltammograms of corannulene and BB-PA were obtained in the solution phase by dissolving them in the electrolyte. The insoluble BB-POPs were dispersed in acetone with polytetrafluoroethylene (PTFE, 5-15 %) as a binder, drop cast onto the gold working electrode and dried. Platinum mesh was used as a counter electrode and potentials were recorded versus Ag/Ag⁺ (0.01M) as a reference electrode. The scan rate was 100 mV.s⁻¹.

2. Synthesis

Monomer synthesis

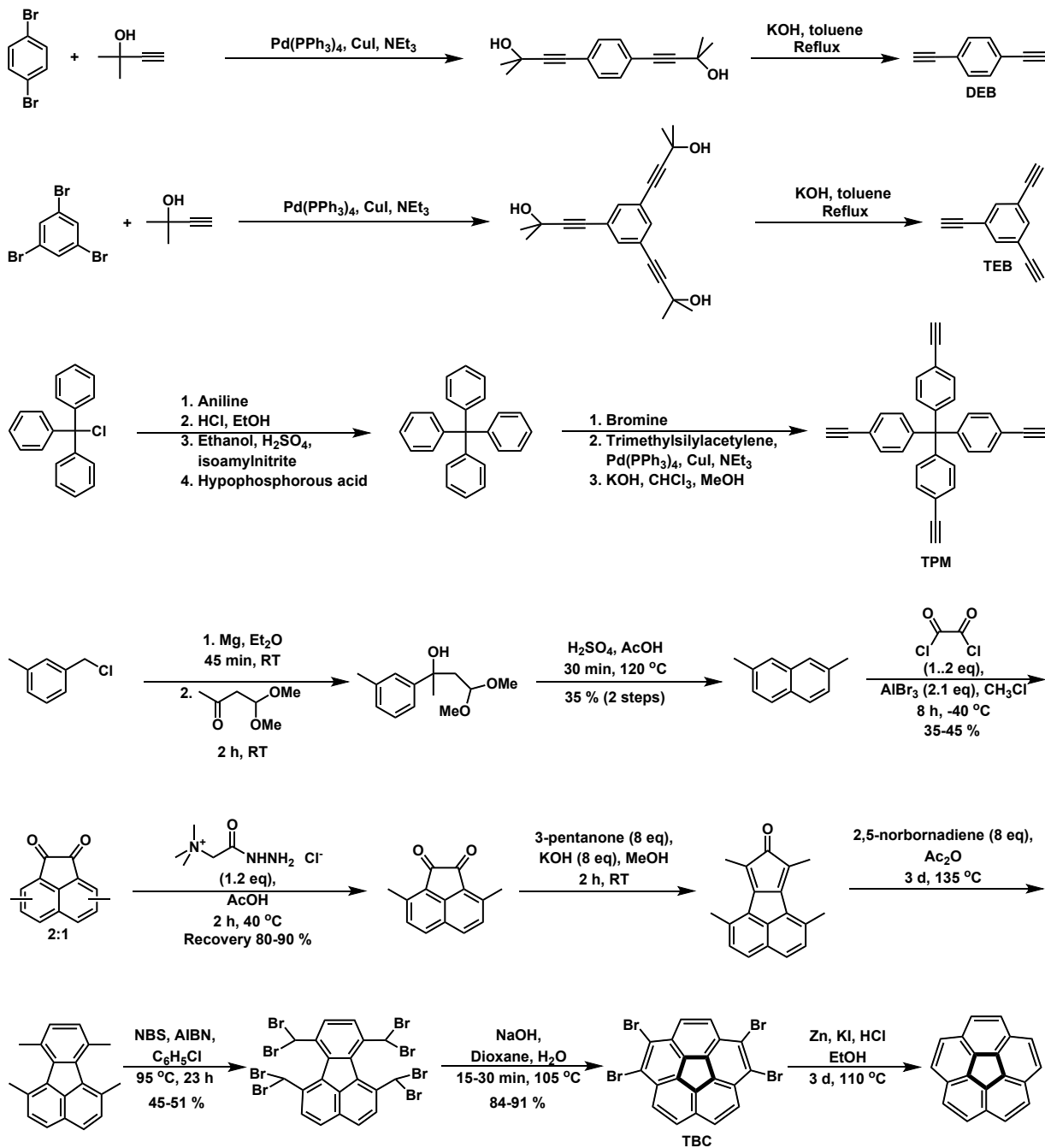


Fig S1: Synthesis of 1,4-diethynylbenzene (**DEB**), 1,3,5-trisethynylbenzene (**TEB**), tetrakis(4-ethynyl)-tetraphenylmethane (**TPM**), and 1,2,5,6-tetrabromocorannulene (**TBC**).^[1, 2, 3, 4, 5]

Model compound

1,2,5,6-Tetra(phenylethynyl)corannulene (**BB-PA**) was prepared using previously described methods.^[6]

Polymer Synthesis

BB-POP-1: To a pressure tube containing **TBC** (40 mg, 0.071mmol) and **DEB** (17.9 mg, 0.142 mmol) were added toluene (2 mL) and Et₃N (4 mL). This was purged with nitrogen for 15 min before Pd(PPh₃)₄ (15.0 mg, 0.014mmol) and CuI (2.6 mg, 0.014 mmol) were added and the tube was sealed. The reaction was then heated at 90 °C for 18 h. After that time a brown solid had formed which was collected by filtration, and washed with CH₂Cl₂ (100 mL) and methanol (100 ml), followed by sonication (20 min) in CH₂Cl₂ twice after which time the solid was collected by filtration. The polymer was then sonicated in 5 mL of hot toluene for five minutes before being filtered. This washing procedure was repeated a total of five times in hot toluene followed by five washings in 5 mL hot DMSO. The solid was finally washed with acetone (100 mL). Yield = 27 mg (77%).

BB-POP-2 To a pressure tube containing **TBC** (40 mg, 0.071mmol) and **TEB** (14.2 mg, 0.094 mmol) were added toluene (2 mL) and Et₃N (4 mL). This was purged with nitrogen for 15 min before Pd(PPh₃)₄ (16.33 mg, 0.014mmol) and CuI (2.76 mg, 0.014 mmol) were added and the tube was sealed. The reaction was then heated at 90 °C for 18 h. After that time a brown solid had formed which was collected by filtration, and washed with CH₂Cl₂ (100 mL) and methanol (100 ml), followed by sonication (20 min) in CH₂Cl₂ twice and then the solid was collected by filtration. The polymer was then sonicated in 5 mL of hot toluene for five minutes before being filtered. This washing procedure was repeated a total of five times in hot toluene followed by five washings in 5 mL hot DMSO. The solid was finally washed with acetone (100 mL). Yield = 25 mg (80%).

BB-POP-3 To a pressure tube containing **TBC** (40 mg, 0.071mmol) and **TPM** (29.4 mg, 0.071 mmol) were added toluene (2 mL) and Et₃N (4 mL). This was purged with nitrogen for 15 min before Pd(PPh₃)₄ (16.33 mg, 0.014mmol) and CuI (2.8 mg, 0.014 mmol) were added and the tube was sealed. The reaction was then heated at 90 °C for 18 h. After that time a brown solid had formed which was collected by filtration, and washed with CH₂Cl₂ (100 mL) and methanol (100 ml), followed by sonication (20 min) with CH₂Cl₂ for twice and filtered. The polymer was then sonicated in 5 mL of hot toluene for five minutes before being filtered. This washing procedure was repeated a total of five times in hot

toluene followed by five washings in 5 mL hot DMSO. The solid was finally washed with acetone (100 mL). Yield = 43 mg, (92%).

3. FT-IR Characterization

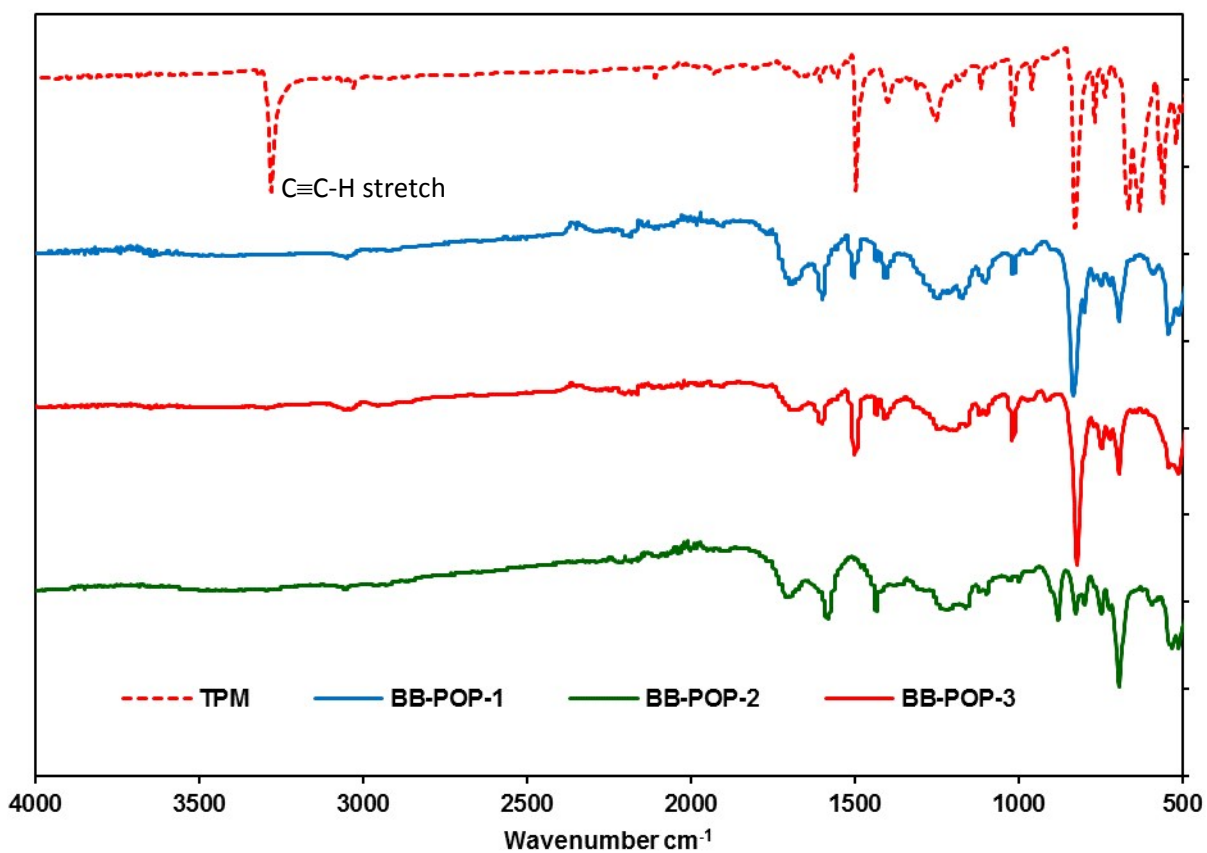


Fig S2: IR spectra of tetrakis(4-ethynyl)-tetraphenylmethane (TPM) and BB-POPs.

4. EDX Data

Table S1: Elemental ratios in BB-POPs based on EDX.

Sample	Weight %			Atomic %		
	C%	Br%	Pd%	C%	Br%	Pd%
BB-POP-1	88.15	10.01	1.84	98.09	1.67	0.23
BB-POP-2	87.50	9.98	2.52	98.00	1.68	0.32
BB-POP-3	91.00	7.47	1.52	98.60	1.22	0.19

5. SEM Images

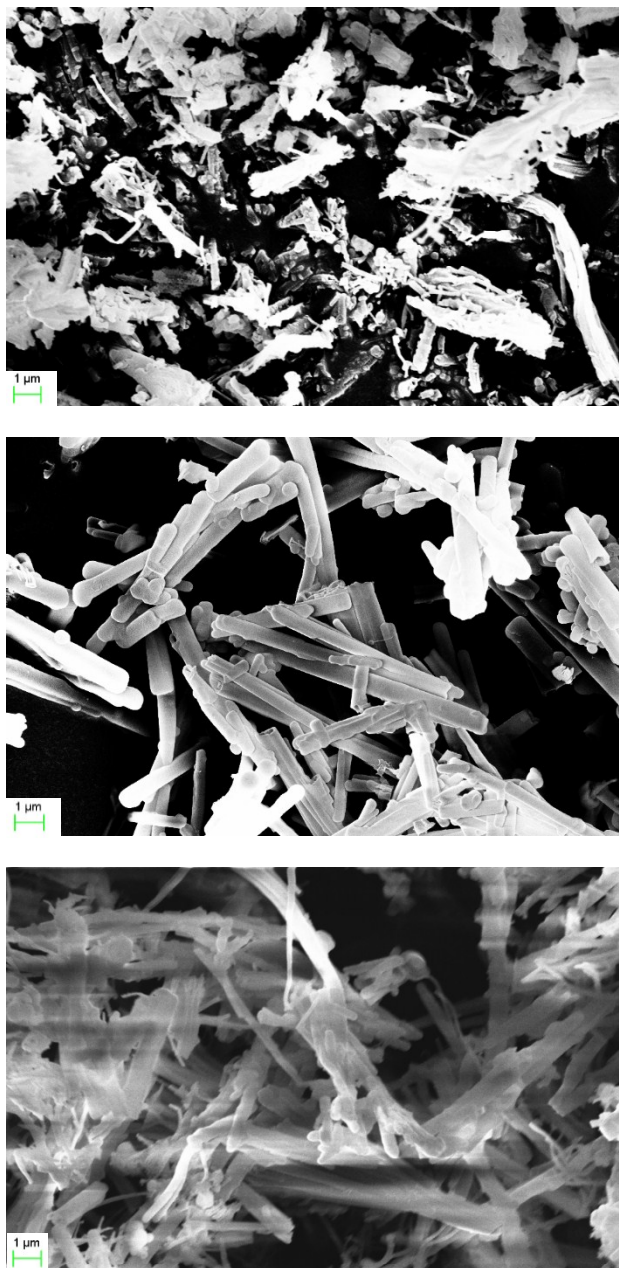


Fig S3: SEM images of BB-POPs: BB-POP-1 (top), BB-POP-2 (middle) and BB-POP-3 (bottom).

6. Thermogravimetric Analysis

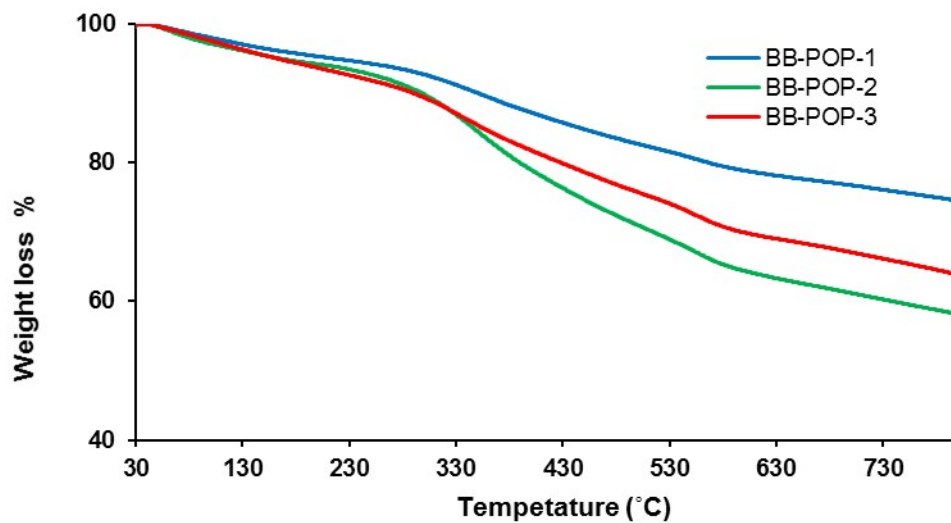


FIG S4: TGA curves of BB-POPs.

7. Powder X-Ray Diffraction Characterization

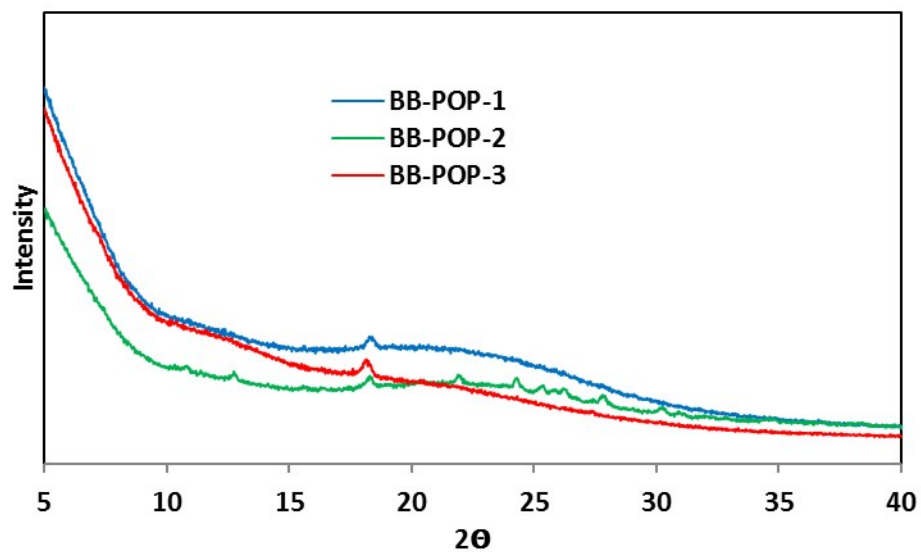


Fig S5: PXRD patterns of BB-POPs.

8. Fluorescence

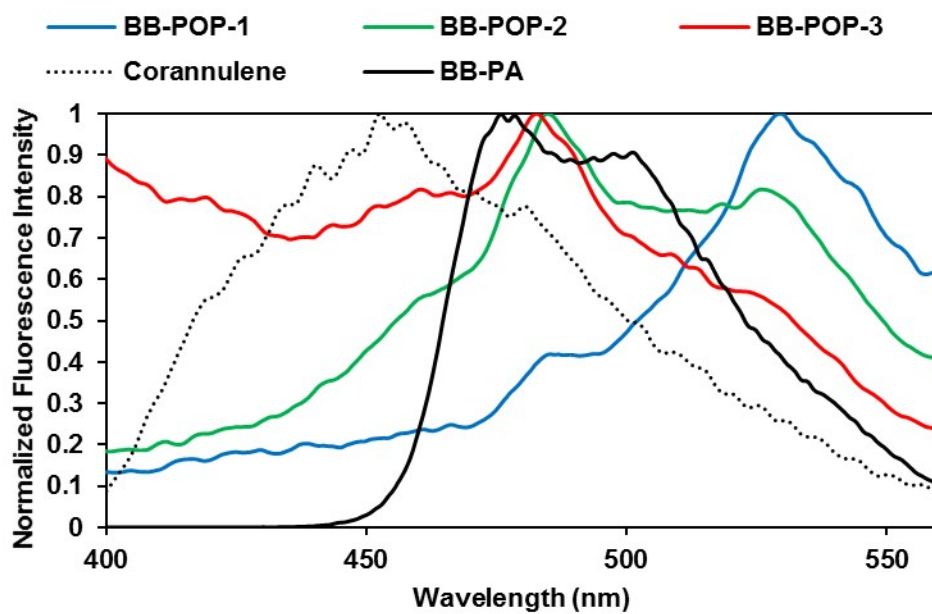


Fig S6: Normalized emission spectra in CH_2Cl_2 with excitation at 300 nm.

9. Pore Analysis and Gas Sorption Isotherms

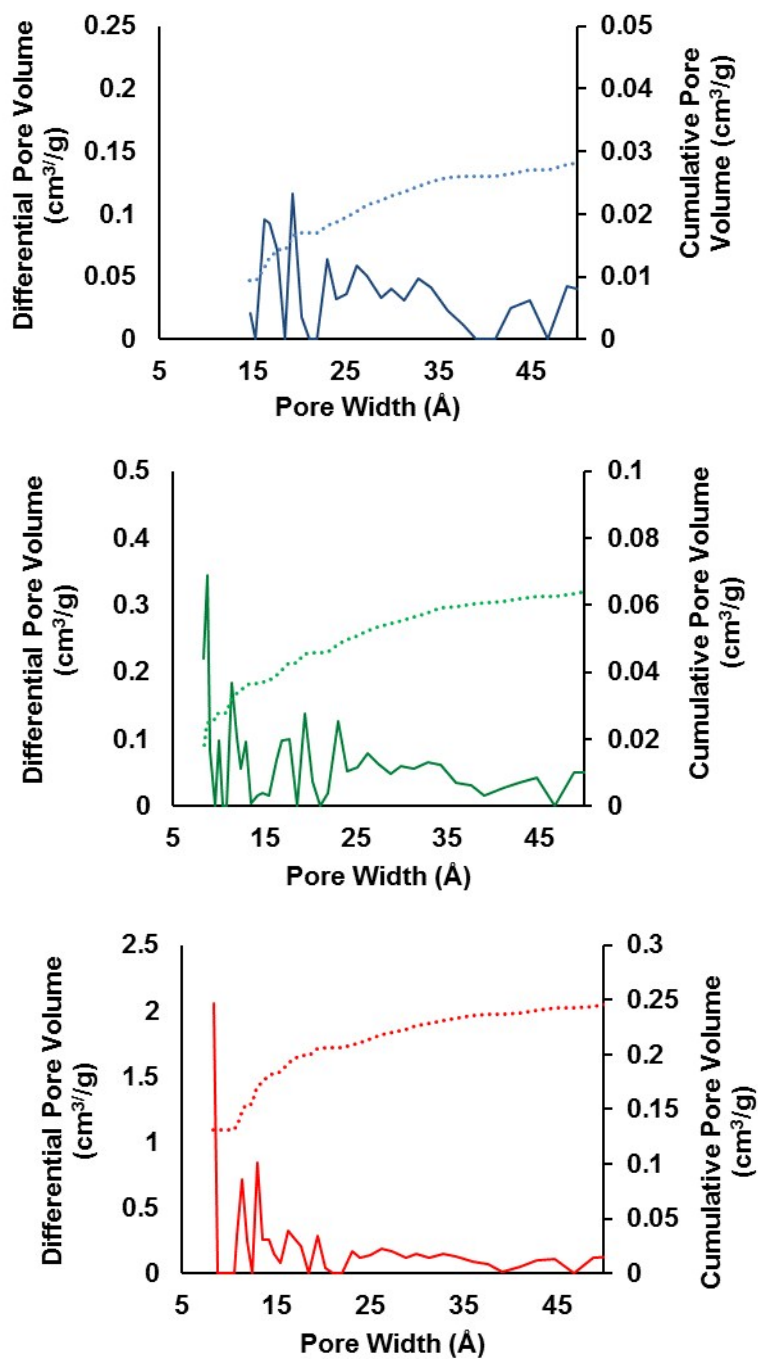


Fig S7: Differential (line) and cumulative (dash) pore size distributions of BB-POP-1 (blue), BB-POP-2 (green), BB-POP-3 (red).

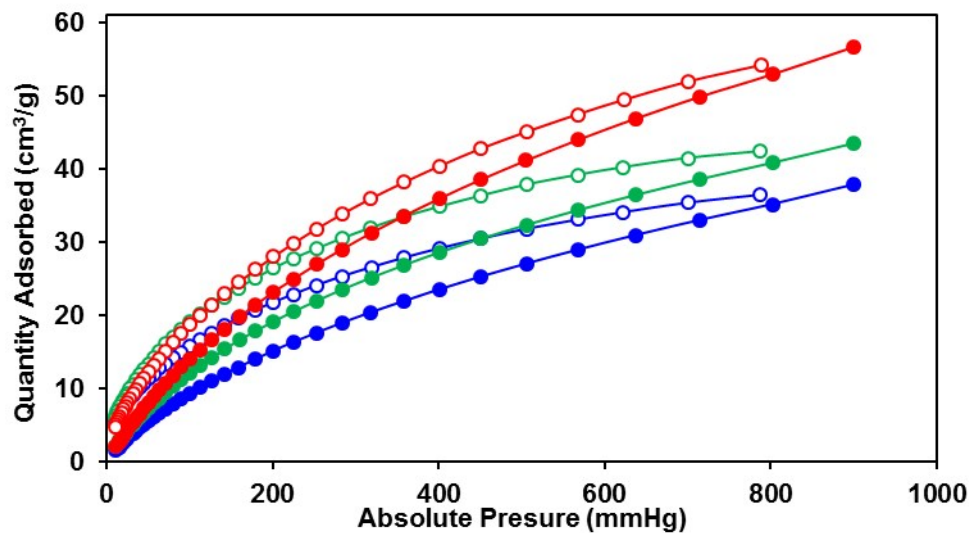


Fig S8: CO₂ adsorption isotherms at 273 K adsorption (filled circles) desorption (open circles) for BB-POP-1 (blue), BB-POP-2 (green) and BB-POP-3 (red).

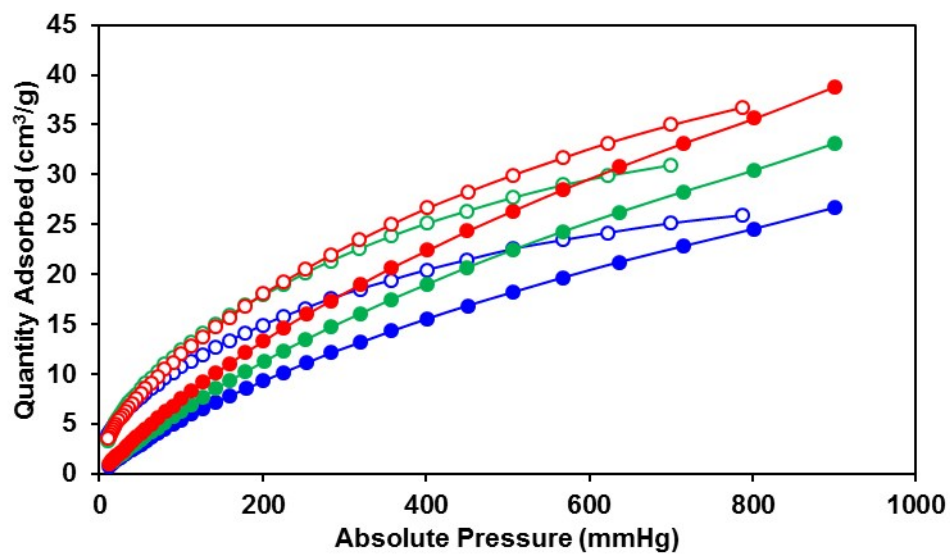


Fig S9: CO₂ adsorption isotherms at 298 K adsorption (filled circles) desorption (open circles) for BB-POP-1 (blue), BB-POP-2 (green) and BB-POP-3 (red).

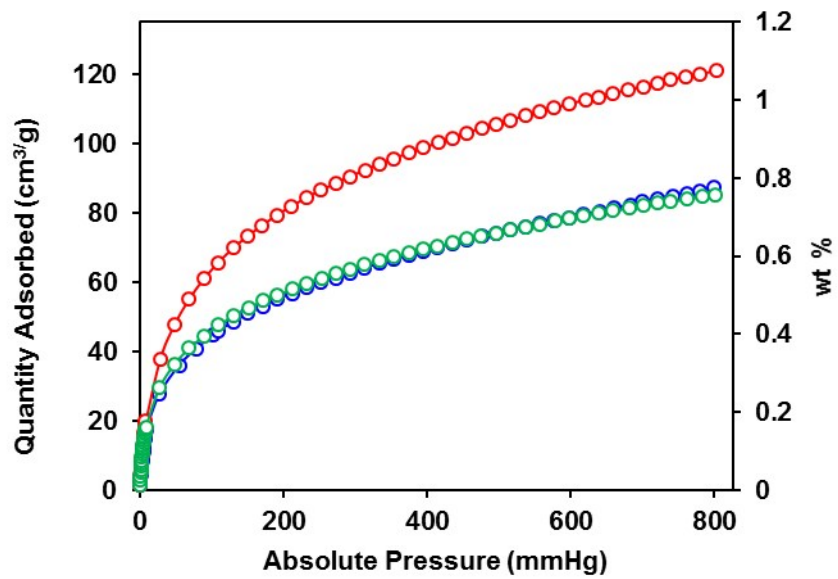


Fig S10: H₂ adsorption isotherms at 77 K for BB-POP-1 (blue), BB-POP-2 (green) and BB-POP-3 (red).

10. Cyclic voltammetry

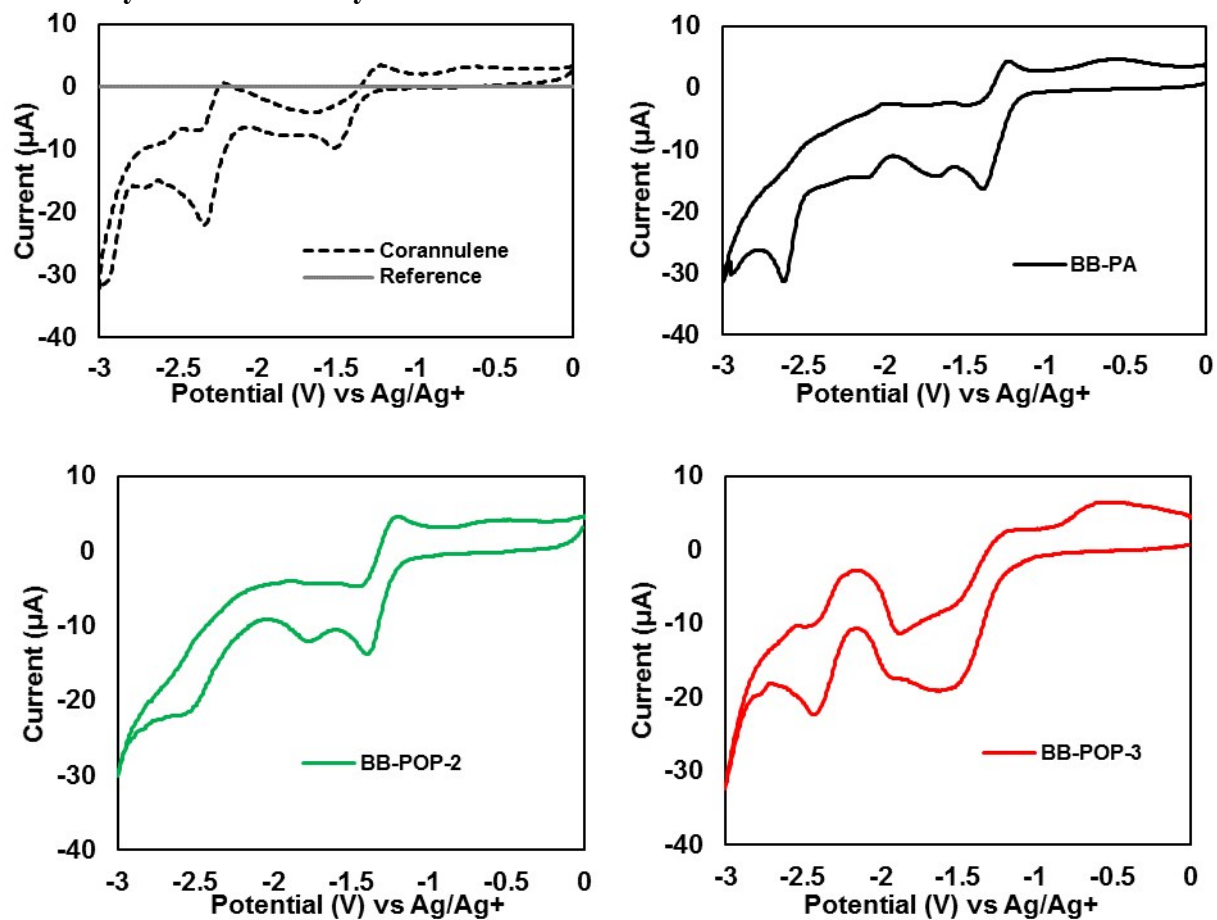


Fig. S11: Cyclic voltammograms of BB-POP-2 and 3, corannulene (1 mM), BB-PA (1 mM) and reference (bare gold electrode) in 0.1 M tetrabutylammonium hexafluorophosphate /DMF using Pt mesh as the counter electrode, Ag/Ag⁺ as the reference electrode and Au as the working electrode.

References

1. A. M. Butterfield, B. Gilomen, J. S. Siegel, *Org. Process Res. Dev.*, 2012, **16**, 664-676.
2. T. Mori, S. Grimme, Y. Inoue, *J. Org. Chem.*, 2007, **72**, 6998-7010.
3. A. Sygula, G. Xu, Z. Marcinow, P. W. Rabideau, *Tetrahedron*, 2001, **57**, 3637-3644.
4. W. Shu, C. Guan, W. Guo, C. Wang, Y. Shen, *J. Mater. Chem.*, 2012, **22**, 3075-3081.
5. P. Pandey, O. K. Farha, A. M. Spokoyny, C. A. Mirkin, M. G. Kanatzidis, J. T. Hupp, S. T. Nguyen, *J. Mater. Chem.*, 2011, **21**, 1700-1703.
6. Y. Wu, D. Bandera, R. Maag, A. Linden, K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.*, 2008, **130**, 10729-10739.