Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for

# A Silver(I) Coordinated Phenanthroline-Based Conjugated Polymer with High Ethylene/Ethane Adsorption Selectivity

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## 1. Materials and methods

Unless otherwise stated, all chemical reagents were commercially available and used without further purification. 2,9-dibromo-1,10-phenanthroline,[S1] 1,4-di-*tert*-butyl-2,5-diiodobenzene,[S2] and 2,9-bis(phenylethynyl)-1,10-phenanthroline[S3] were synthesized following the published procedures. All reactions were conducted under nitrogen atmosphere.

Flash column chromatography was performed by using a 100-150 times weight excess of flash silica gel 32-63 μm from Dynamic Absorbants Inc. Fractions were analyzed by TLC using TLC silica gel F254 250 μm precoated-plates from Dynamic Absorbants Inc.

NMR spectra were taken on Inova 400 and Inova 500 spectrometers. Solid-state cross polarization magic angle spinning (CP/MAS) NMR spectra were recorded on an Inova 400 NMR spectrometer. Deuterated solvents were purchased from Cambridge Isotope Laboratories (Andover, MA) and used as received.

The FT-IR spectra were obtained in the form of KBr pellets, using a Thermo Nicolet Avatar-370 spectrometer.

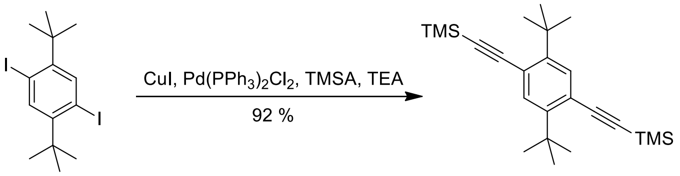
Elemental analyses were taken at Huffman Laboratories, Inc.

Thermogravimetric analysis (TGA) was performed in Pyris 7 TGA (Perkin Elmer) by heating the sample under an atmosphere of nitrogen from 50 $^{o}$C to 850 $^{o}$C at 10 $^{o}$C/min.

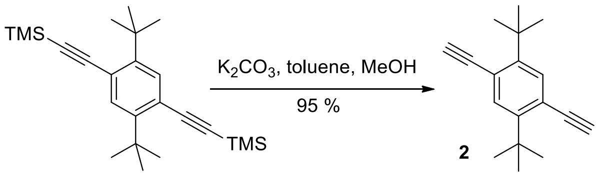
Scanning Electron Microscopy images (SEM) were recorded using a JSM-6480LV (LVSEM) at 5.0 kV.

Gas adsorption measurements were performed using a customized apparatus as described in Section 7.

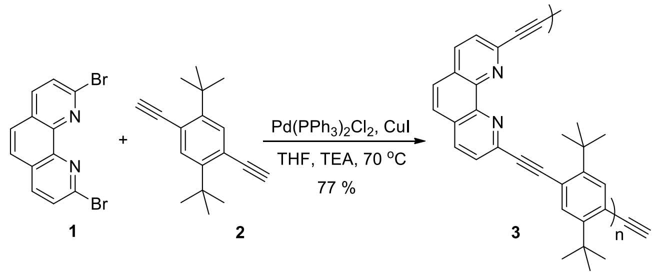
## 2. Synthetic procedures



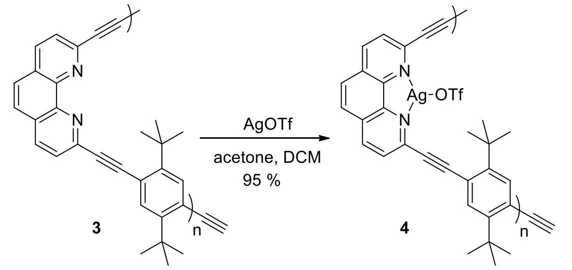
**((2,5-Di-*tert*-butyl-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane):** 1,4-Di-*tert*-butyl-2,5-diiodobenzene (1.00g, 2.26 mmol), $Pd(PPh_3)_2Cl_2$ (127 mg, 0.18 mmol), and CuI (4.3 mg, 0.023 mmol) were added into a Schlenk tube. Triethylamine (45 mL) was added, followed by 2-methyl-but-3-yn-2-ol (666 mg, 0.97 mL, 6.79 mmol). The mixture was stirred under nitrogen at 50 °C for 10 hours. The mixture was diluted with dichloromethane (50 mL) and washed with water (3 x 50 mL). The crude product was purified by flash column chromatography using hexanes as the eluent to yield ((2,5-di-*tert*-butyl-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) as a white solid (800 mg, 92 %): $^1$H NMR (500 MHz, $CDCl_3$): δ 7.43 (s, 2H), 1.47 (s, 18H), 0.25 (s, 18H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 149.0, 132.8, 121.4, 107.2, 101.5, 35.3, 29.8, -0.2.



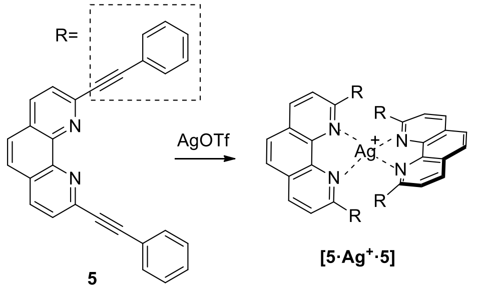
**1,4-Di-*tert*-butyl-2,5-diethynylbenzene (2):** A mixture of ((2,5-di-*tert*-butyl-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (798 mg, 2.09 mmol), $K_2CO_3$ (2.88 g, 20.9 mmol), toluene (50 mL), and methanol (75 mL) was stirred under nitrogen at room temperature for 1 hour. The solvents were removed and hexanes was added and washed with water. The crude product was purified by flash column chromatography using hexanes as the eluent to provide 1,4-di-*tert*-butyl-2,5-diethynylbenzene as a white solid (472 mg, 95 %): $^1$H NMR (500 MHz, $CDCl_3$): δ 7.50 (s, 2H), 3.47 (s, 2H), 1.48 (s, 18H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 149.1, 133.5, 120.8, 85.3, 84.3, 35.3, 29.9.



**Polymer 3:** 2,9-dibromo-1,10-phenanthroline (**1**, 154 mg, 0.46 mmol), 1,4-di-*tert*-butyl-2,5-diethynylbenzene (**2**, 108 mg, 0.46 mmol), $Pd(PPh_3)_2Cl_2$ (25 mg, 0.036 mmol), and CuI (0.9 mg, 0.0046 mmol) were added into a Schlenk tube, followed by TEA (1.1 mL) and THF (7.5 mL). The mixture was stirred under nitrogen at 70 °C for 10 hours. The solvents were removed and dichloromethane (10 mL) was added. The mixture was filtered and the solid was washed with dichloromethane (10 x 10 mL), water (10 x 5 mL), and acetone (5 x 5 mL), and dried *in vacuo* to give polymer **3** as a brown solid (151 mg, 77 %): Elemental analysis for $[(C_{30}H_{26}N_2)(H_2O)_{1.8}]_n$ Calcd.: C: 80.61%; H: 6.67%; N: 6.27% Found: C: 80.56%; H: 6.08%; N: 5.94%.



**Polymer 4:** A solution of silver trifluoromethanesulfonate (AgOTf, 29 mg, 0.11 mmol) in acetone (2 mL) was dropped into a suspension of polymer **3** (48 mg, 0.11 mmol) in dichloromethane (5 mL). The mixture was stirred under exclusion of light for 15 minutes and the solvents were removed. The solid mixture was washed with acetone (5 x 5 mL). The brown solid was dried in vacuo to afford polymer **4** (73 mg, 95 %): Elemental analysis for $[(C_{30}H_{26}N_2)(H_2O)_{0.5}(AgCF_3O_3S)_{0.75}]n$: Calcd.: C, 59.93%; H, 4.42%; N, 4.54%; Ag, 13.1%, Found: C, 59.77%; H, 4.52%; N, 4.30%; Ag, 13.3%.



**Complex [5·Ag$^+$·5]:** To a solution of 2,9-bis(phenylethynyl)-1,10-phenanthroline (**5**, 54 mg, 0.14 mmol) in dichloromethane (4 mL) was dropped a solution of silver trifluoromethanesulfonate (18 mg, 0.07 mmol) in acetone (2 mL). The mixture was stirred under exclusion of light for 15 minutes and the solvents were removed. The white solid was dried in vacuo (72 mg, 100 %): $^1$H NMR (500 MHz, acetone-d$_6$): δ 8.75 (d, *J* = 8.3 Hz, 1H), 8.21 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.3 Hz, 2H), 6.78 (s, 2H); $^{13}$C NMR (100 MHz, acetone-d$_6$): δ 143.2, 138.9, 131.0, 129.6, 128.8, 128.2, 127.5, 127.2, 120.5, 89.3.

## 3. FT-IR

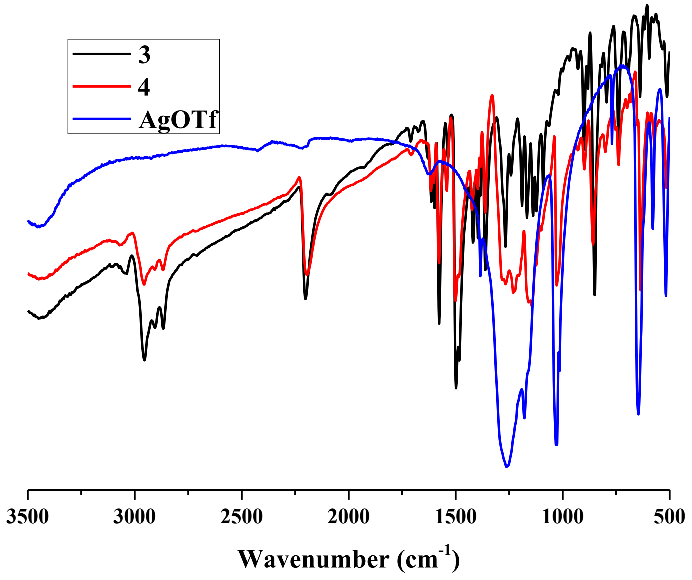


**Figure S1.** FT-IR spectra of **3**, **4** and AgOTf.

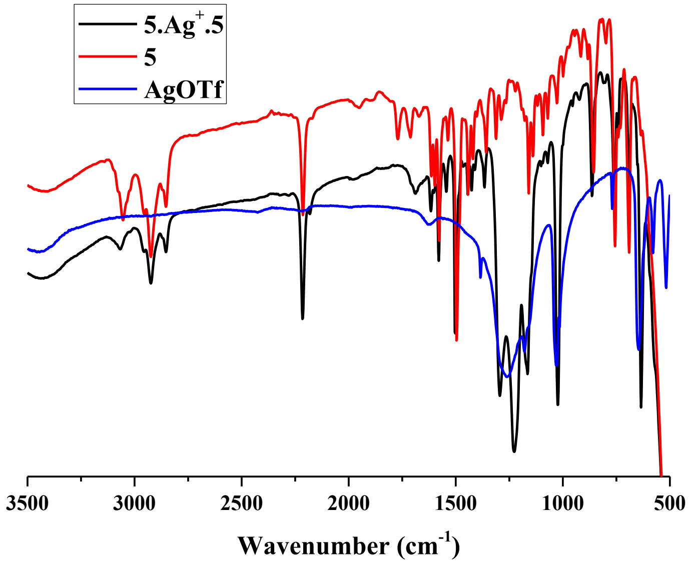


**Figure S2.** FT-IR spectra of **5**, [**5**·Ag$^+$·**5**] and AgOTf.

## 4. NMR traces

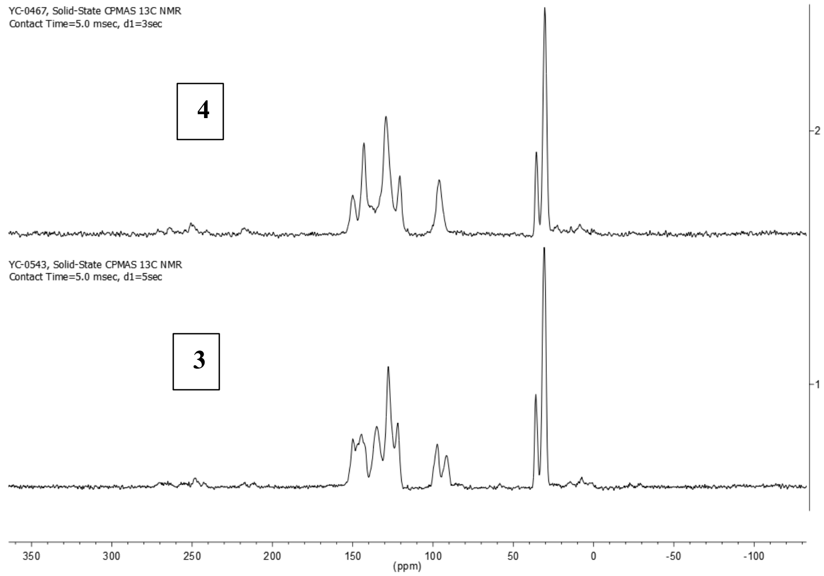


**Figure S3.** Solid-State $^{13}$C CP-MAS NMR spectra of **3** and **4**.

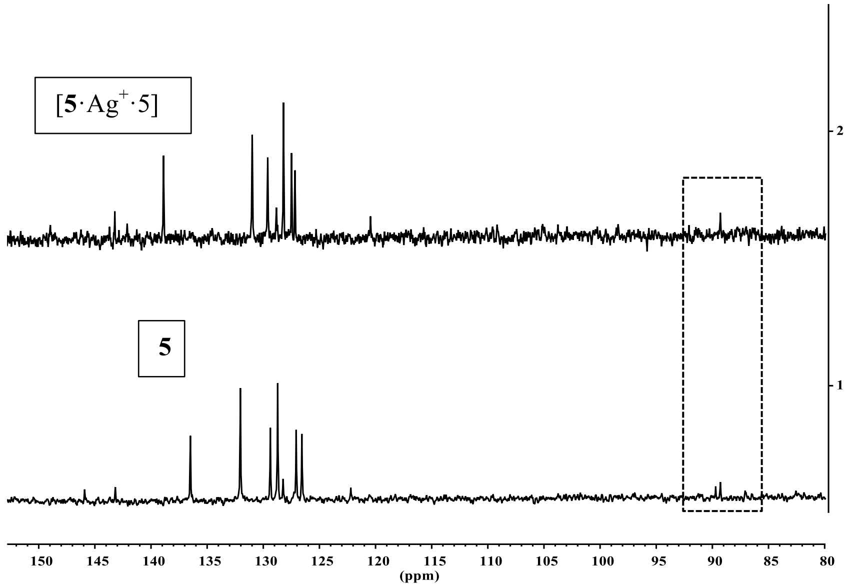


**Figure S4.** $^{1}$C NMR spectra of **5** and [**5**·Ag$^{+}$·**5**] in acetone-d$_6$.

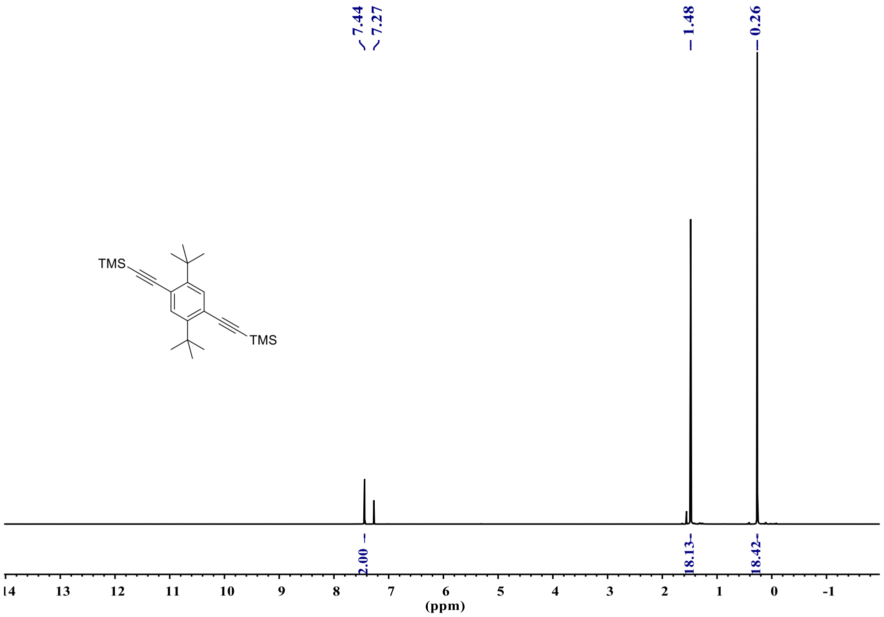


**Figure S5.** $^{1}$H NMR spectrum of ((2,5-di-*tert*-butyl-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane).

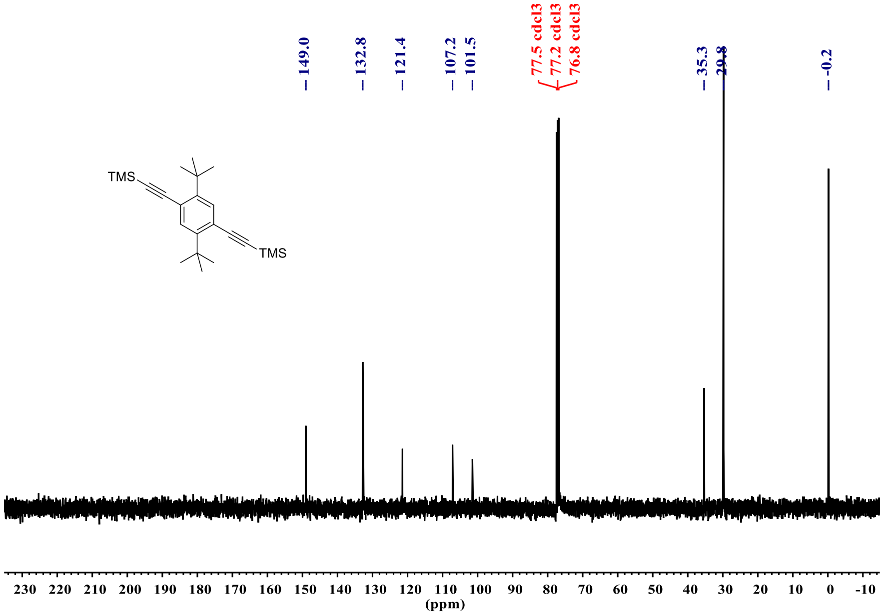


**Figure S6.** $^{13}$C NMR spectrum of ((2,5-di-*tert*-butyl-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane).

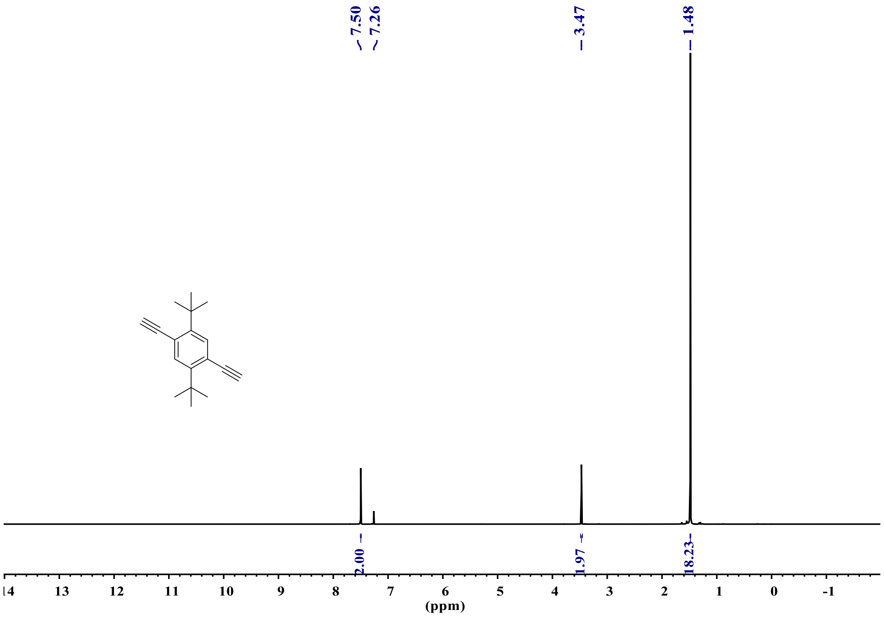


**Figure S7.** $^1$H NMR spectrum of 1,4-di-*tert*-butyl-2,5-diethynylbenzene.

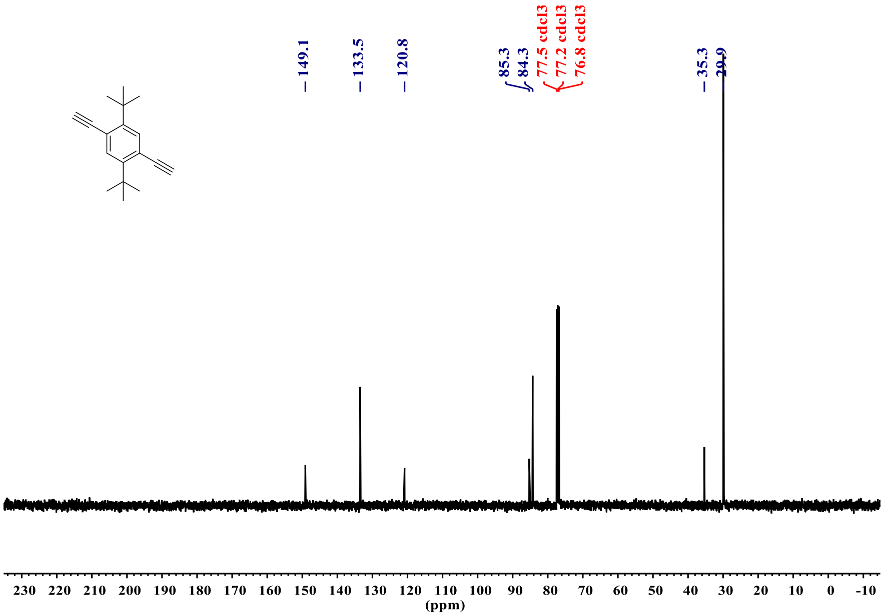


**Figure S8.** $^{13}$C NMR spectrum of 1,4-di-*tert*-butyl-2,5-diethynylbenzene.

## 5. TGA

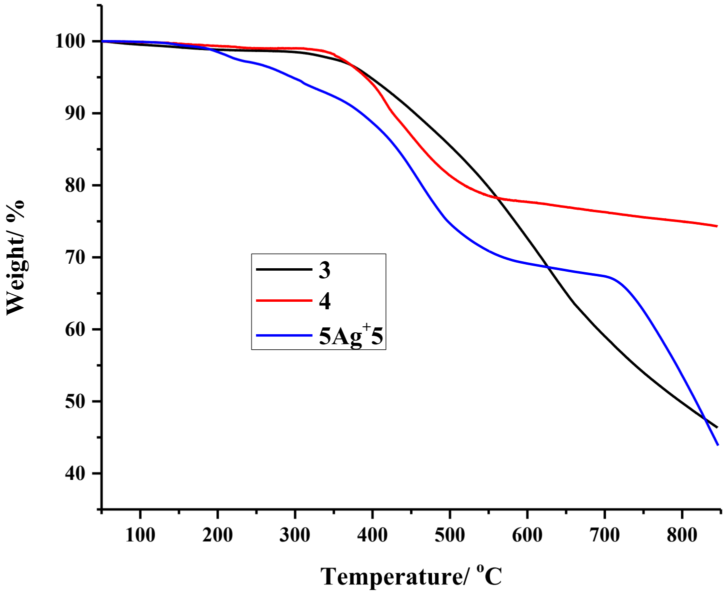


**Figure S9.** TGA profile of **3**, **4** and [**5**·Ag$^+$·**5**].

## 6. SEM

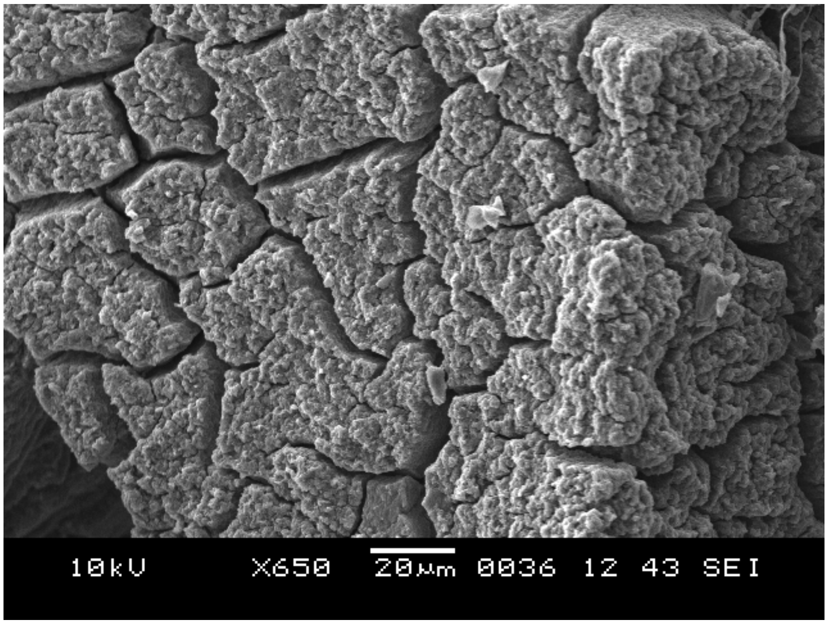


**Figure S10.** SEM image of **3**.

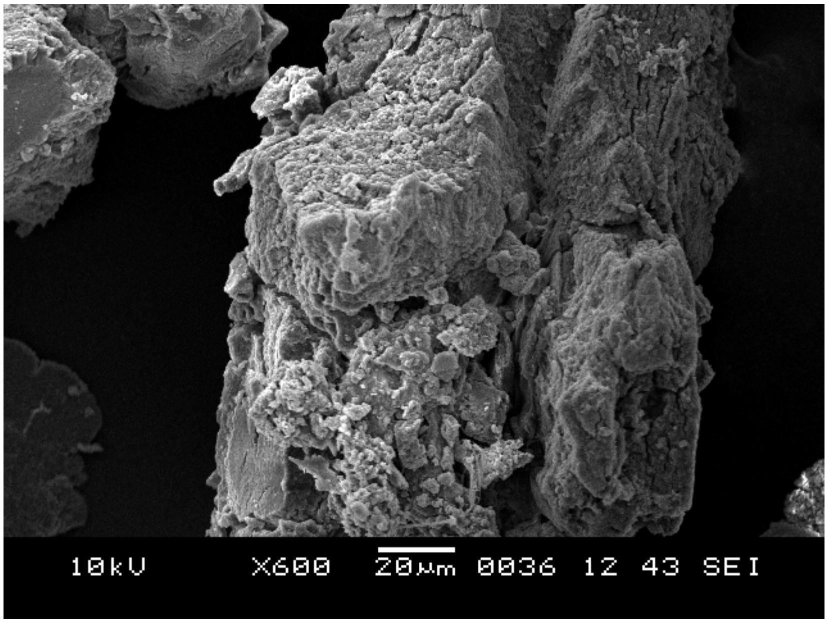


**Figure S11.** SEM image of **4**.

## 7. Gas Adsorption Measurements

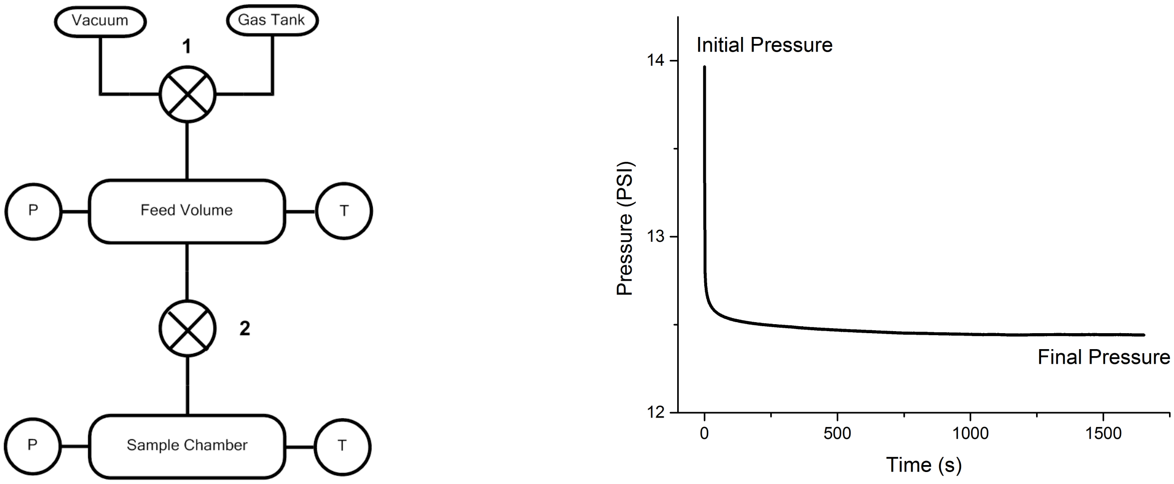


**Figure S12.** Left: The experimental set up for measurement of gas adsorption using the pressure drop method. Where 'P' and 'T' are pressure and temperature sensors, respectively; circles with crosses denote valves and the volume of the sample chamber is known. Right: An example of the pressure vs. time data obtained from the experiment.

### Experimental Method

To ensure a high surface area, increasing the speed of the measurements, the samples were ground into a fine powder using a mortar and pestle. A known weight of the powder was then placed into the sample chamber. To remove any residual gases from the samples, valves 1 and 2 were opened to dynamic vacuum (<0.5 torr) for 18 hours. Immediately after degassing, valve 2 was closed and the feed volume filled with approximately 1 bar (14.5 psi) of the gas to be measured. Valve 2 was then opened for 1 second, filling the sample chamber with the gas of interest. Valve 2 was then closed and the pressure decrease in the sample chamber was measured over time until a constant pressure ($P_f$) was observed. The pressure difference, corrected for the empty cell, (Equation 1) was used to calculate the amount of gas adsorbed by the sample in units of $mol_{gas}$ (Equation 2). The amount of gas adsorbed was then normalised by the amount of sample. Each measurement was repeated 3 times and the average values and standard deviations were reported.

$$\Delta P = P_i - P_f - \Delta P_{Blank}$$

$$\Delta P_{Blank} = P_{i(empty)} - P_{f(empty)}$$

Equation 1: $P_i$ = the initial pressure (time zero); $P_f$ = the final pressure (time final).

$$n_{gas} = \frac{\Delta P \cdot V}{R \cdot T}$$

Equation 2: $n_{gas}$ = moles of gas adsorbed; V = volume of the sample chamber; R = the ideal gas constant; T = temperature of sample chamber.

**Table S1.** Ethylene/ethane gas adsorption of compounds studied in this work. Note that the selectivity range is derived from the standard deviation of the adsorption measurements.

| Adsorbent | $C_2H_4$ uptake (mmol/g) | $C_2H_6$ uptake (mmol/g) | Ideal selectivity |
|---|---|---|---|
| **3** | 0.41±0.04 | 0.45±0.05 | 0.9 |
| **4** | 5.04±0.2 | 0.34±0.1 | 14.8 |
| [**5**·$Ag^+$·**5**] | 0.20±0.01 | 0.015±0.0001 | 13.3 |

## 8. References

S1. T. Ishi-i, R. Hirashima, N. Tsutsumi, S. Amemori, S. Matsuki, Y. Teshima, R. Kuwahara and S. Mataka, *J. Org. Chem.* 2010, **75**, 6858.

S2. C. E. Reck and C. H. Winter, *Organometallics* 1997, **16**, 4493.

S3. M. Sjoegren, S. Hansson, P. O. Norrby, B. Aakermark, M. E. Cucciolito, A. Vitagliano, *Organometallics* 1992, **11**, 3954.