

Supporting Information for

Tuning Surface Accessibility and Catalytic Activity of Au Nanoparticles through Immobilization within Porous-Organic Polymers

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Experimental Procedure

All reagents were commercial grade used as received unless otherwise noted. Air and moisture sensitive reactions were conducted under nitrogen atmosphere using Schlenk line. Solvents, catalysts, and common chemicals were purchased from Sigma-Aldrich or Fisher Scientific-UK. Brominated aromatics were purchased from Combi-Blocks.. Nitrogen and CO₂ gases for sorption were purchased from Airliquide (N₂ and H₂ AlphaGaz2 (99.999%) and CO₂ (99.995%)). Gas sorption analysis was performed on Micromeritics **ASAP2020** and the variable temperature CO₂ isotherms were recorded in insulated dewar connected to **LAUDA RA-8** circulating chiller. UV-Vis spectra were acquired on ThermoScientific **Evolution 600** UV-Vis spectrophotometer equipped with integrating sphere for solids. Infra-red absorption spectra were recorded on ThermoScientific **Nicolet is-10**. Synthetic reactions were performed under nitrogen atmosphere in oven-dried glassware. Other reagents: 1,4-diethynylbenzene (96%, Sigma Aldrich); 1,3,5-triethynylbenzene, (98%, Alfa-Aesar); copper(I) iodide (CuI, 98%, Acros Organics); bis(triphenylphosphine)palladium(II) dichloride, (98%, Sigma Aldrich); triethylamine (Chromanorm®, HPLC grade, VWR); methanol (MeOH, HPLC grade, Fisher); absolute ethanol (EtOH, HPLC grade, Sigma Aldrich); H₂AuCl₄·hydrate Pd(PPh₃)₂Cl₂, (98%, Sigma Aldrich).

Synthesis of Tetrakis(p-bromophenyl)methane: The synthesis was done according to the reported procedure (M. Ng, D. Craig, J. Harper, L. van-Eijck and J. Stride, Chem.–Eur. J., **2009**, *15*, 6569-6572).

Solid-state NMR: Solid-state ¹³C 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 ¹H channel and 62.5 kHz field on the ¹³C 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.

SEM images were taken on FEI-NovaNano SEM equipped with EDAX - Octane Silicon Drift Detector, TEAM™ EDS Analysis Systems for EDX analysis.

Synthesis of the Citrate-capped gold nanoparticles:

In a 250 ml glass reagent bottle, $\text{H}(\text{AuCl}_4)\cdot\text{H}_2\text{O}$ (88 mg, 0.245 mmol) was dissolved in deionized MilliQ water (160 ml). The solution was then heated to boiling (97 °C) while stirring. Tri-sodium citrate (266 mg, 0.904 mmol) was dissolved in deionized MilliQ water (35 ml) and added in one shot to the boiling solution of $\text{H}(\text{AuCl}_4)\cdot\text{H}_2\text{O}$. The colour changed from yellow to faint yellow to colourless to grey to blue to violet to wine red within 5 minutes. The heater was then turned off after 5 minutes and stirring was continued for 15 minutes, the colour remained wine red. After cooling to room temperature, solution total volume was adjusted to 250 mL by addition of deionized MilliQ water, the storage bottles were closed and stored in the refrigerator at 4°C as stock solution of colloidal gold nanoparticles.

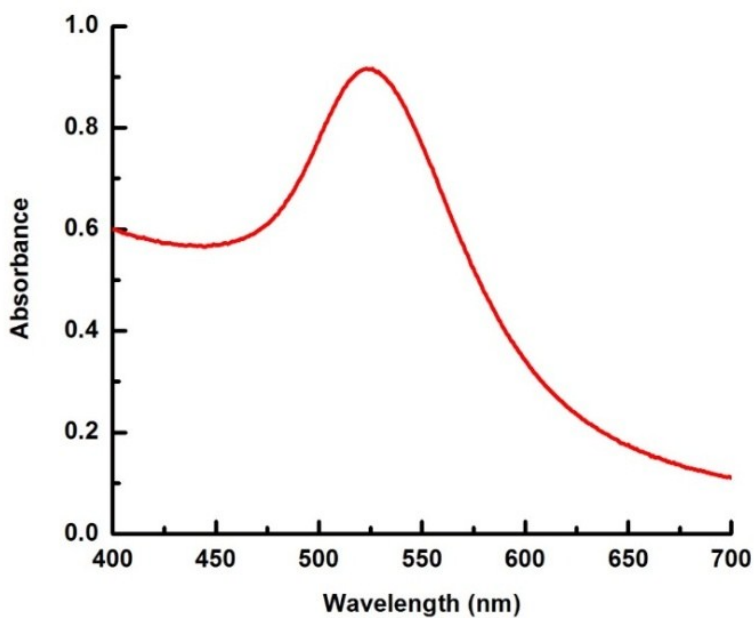


Figure S1: UV-vis spectrum of prepared citrate-capped gold nanoparticles solution.

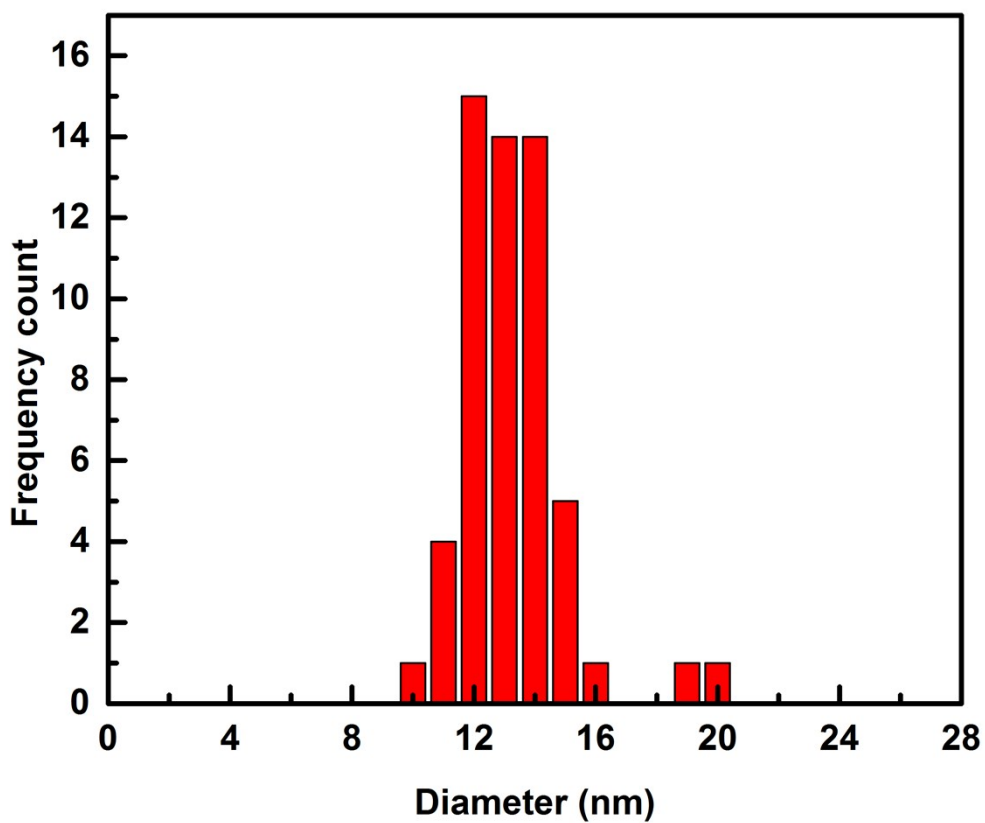
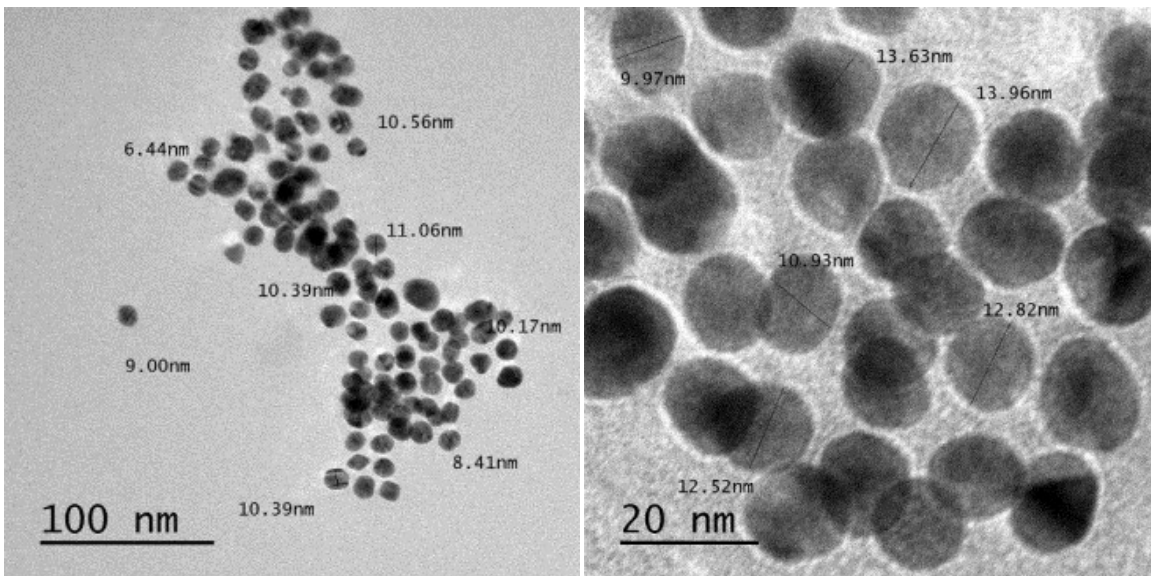


Figure S2. TEM images of prepared citrate-capped gold nanoparticles and size distribution histogram.

Synthesis of 1:

To a colloidal solution of citrate-capped gold nanoparticles, in a 125 mL round bottom flask, (20 mL, ~0.02 mmol Au) was added 10 mL of DMF. To this suspension was then added 4-bromothiophenol (0.25 mL of DCM solution, 0.0025 mmol), the Au NPs were then transferred to the organic layer as the mixture was subjected to evaporation under reduced pressure at 70°C until the final volume was reduced to 6 mL. Additional DMF was added to arrive at a total volume of 10 mL followed by addition of 2 mL of Et₃N. The mixture was degassed through three freeze-pump-thaw cycles, and kept under nitrogen. To the above solution was added 0.233 mL DMF solution containing total of **1,4-diethynylbenzene** (0.15 mg, 0.00125 mmol), **CuI** (0.19 mg), **Pd(PPh₃)₂Cl₂** (0.025 mg), **PPh₃** (0.037 mg). The vessel was then closed by a teflon screw cap and the mixture heated at 80°C for 48h to result in black precipitate and colourless solution. The cross-linked gold nanoparticles prepared as above was centrifuged, washed with DMF, followed by DCM and kept under DCM for guest and solvent exchange. Elemental analysis: C(26.05%), H (3.4%).

The N₂ sorption isotherm for **1** was measured at 77K, however the solid did not show detectable uptake of hydrogen at 77K.

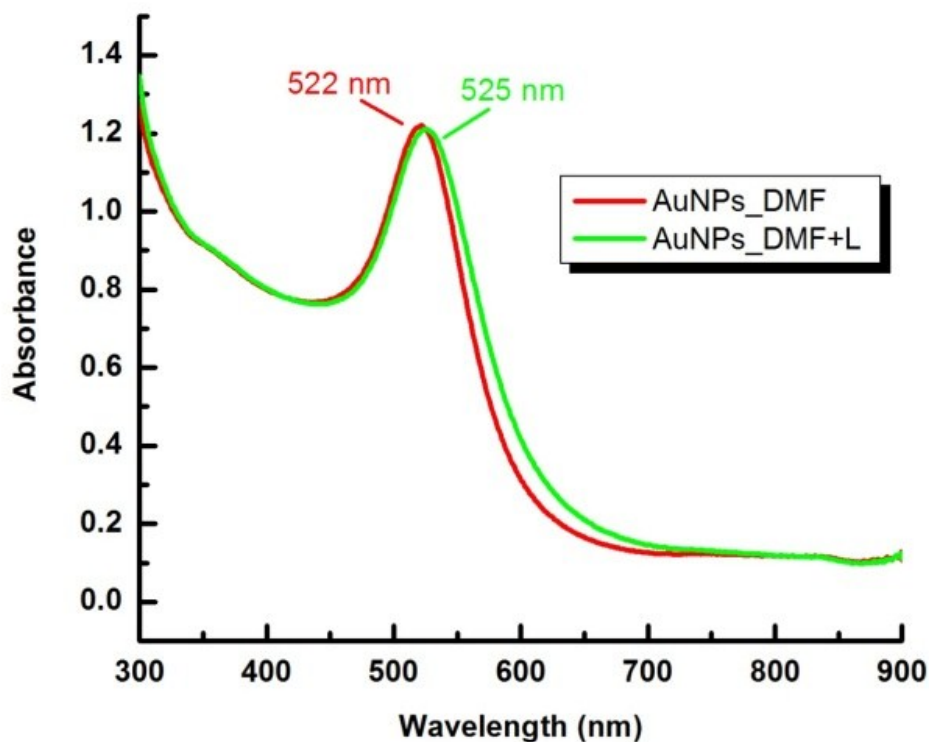


Figure S3. UV-VIS spectra of AuNPs in DMF/water before (red) and after (green) 4-bromothiophenol (ligand) addition

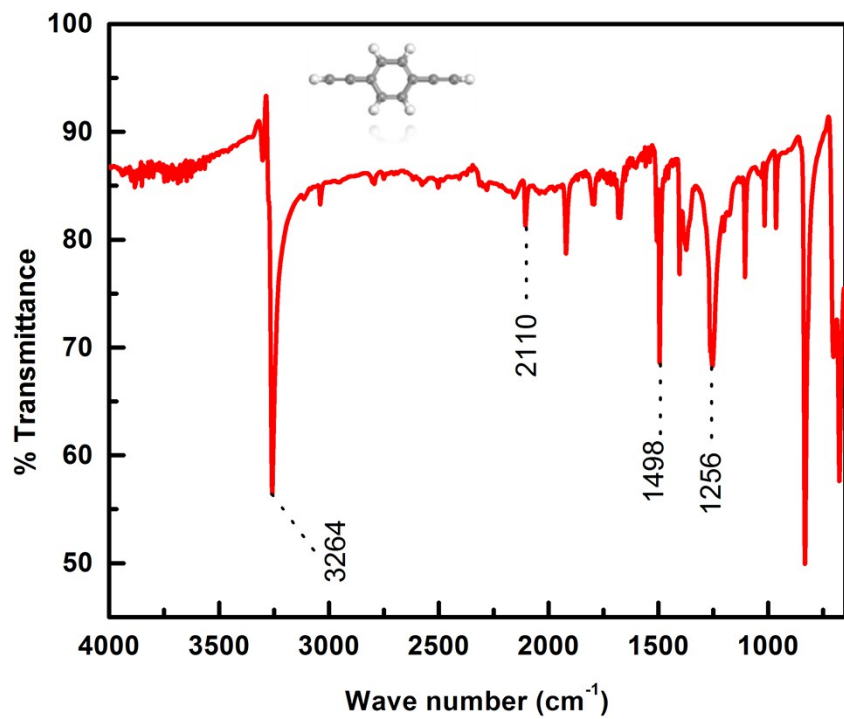


Figure S4. ATR-FTIR spectrum of 1,4-diethynylbenzene.

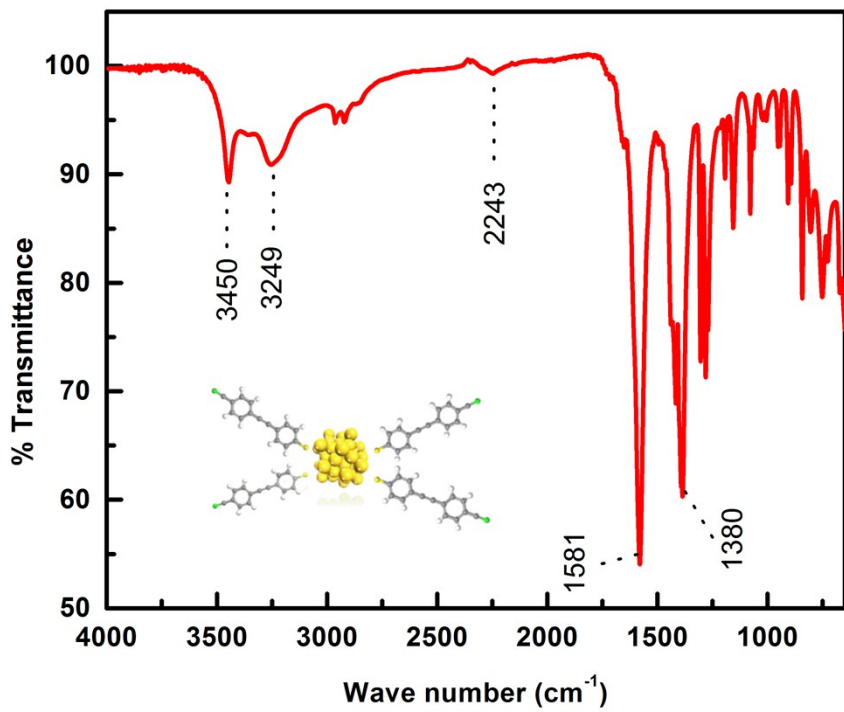


Figure S5. ATR-FTIR spectrum of 1.

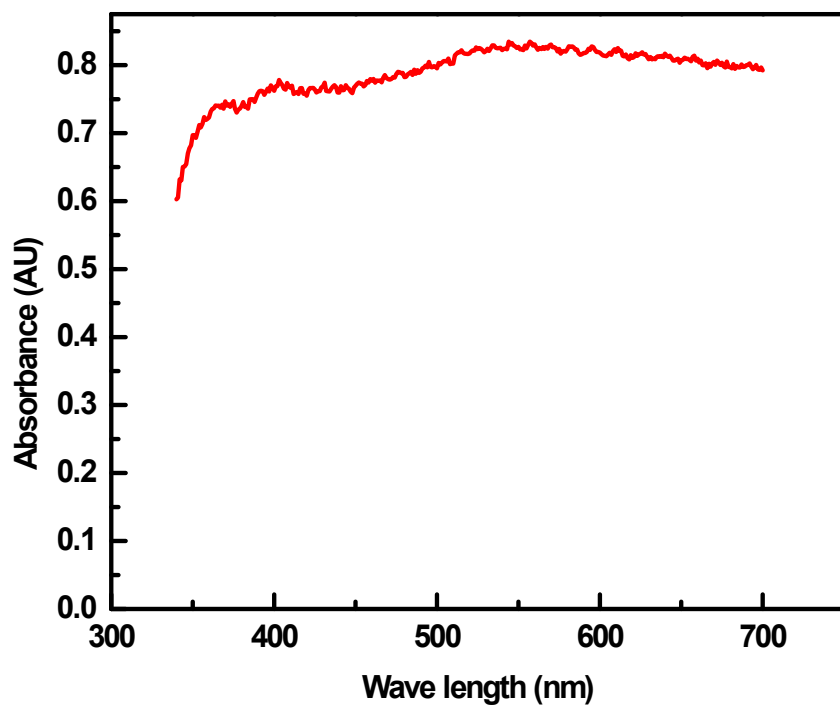


Figure S6. UV-Vis spectrum of 1.

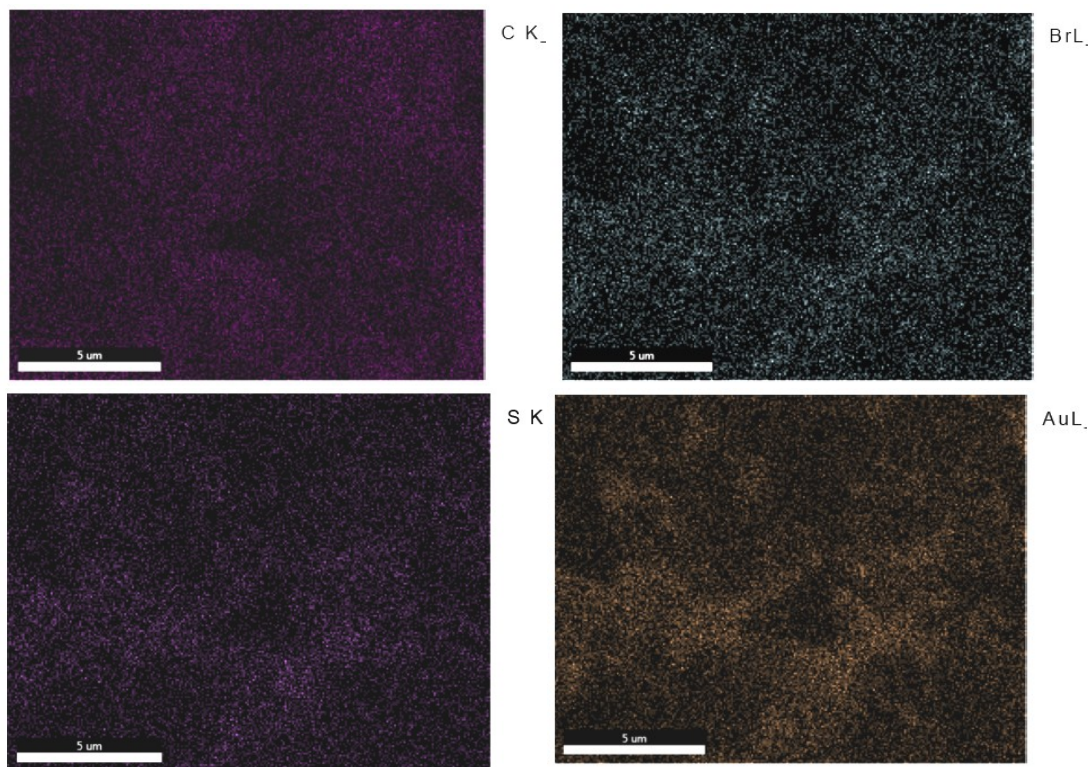
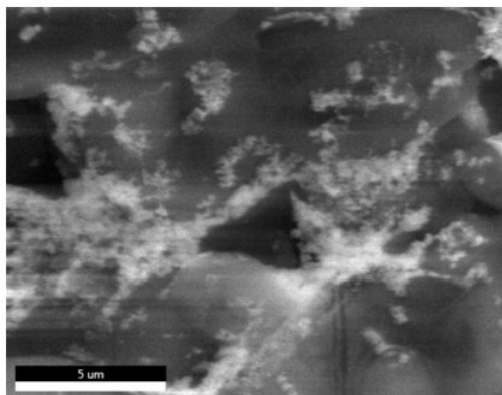
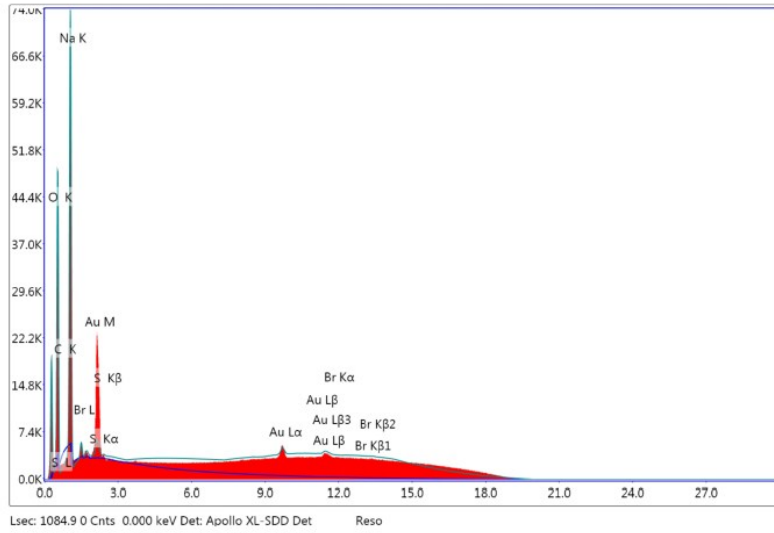


Figure S7: SEM image of **1** (top), and Energy-dispersive X-ray spectroscopy (EDX) maps showing the elemental distribution of C, Br, S, and Au.

Phase: NaK/O K/AuL/C K/S K



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	13.47	34.78	116.5	0
O K	19.76	38.31	321.7	0
NaK	13.68	18.45	503.8	0
BrL	0.08	0.03	3	0.15
S K	0.1	0.1	6.1	0.1
AuL	52.92	8.33	225.9	0

Figure S8. EDX elemental analyses results for compound 1.

Synthesis of 2:

In a 125 mL round bottom flask a colloidal solution of citrate-capped gold nanoparticles (25 mL, 0.025 mmol Au) was added, followed by 10 mL DMF solution of **4-bromothiophenol** (2.67 mg, 0.014 mmol) and the mixture was mixed thoroughly. Most of the aqueous phase was removed under reduced pressure at 80°C in a rotary evaporator, the final mixture volume was 7 mL, and extra DMF was added to bring the final volume to 30 mL. To this solution was added 2 mL of **triethylamine**. The solution was transferred to a 100 mL pressure vessel, cooled in liquid nitrogen bath, degassed through three freeze-pump-thaw cycles and maintained under nitrogen atmosphere. To this prepared solution was added **tris(4-bromotriphenyl) amine** (96.4 mg, 0.2 mmol), **1,3,5-triethynylbenzene** (37 mg, 0.24 mmol), **CuI** (5 mg, 0.026 mmol), **Pph3** (5 mg, 0.019 mmol) and **PdCl₂(Pph₃)₂** (10 mg, 0.014 mmol) and the tube sealed with a Teflon screw under flow of nitrogen. The reaction mixture was then placed in an oil bath maintained at 90°C. After 4h, a deep-orange precipitate formed, filtered through a sintered glass funnel, then washed with DMF, water, and DCM and then kept under MeOH at room temperature for 3 days for guest exchange. The dry weight of the product was found to be 91 mg. Elemental Analysis: C, 70.16%; H, 3.49%; N, 3.83%; S, 0.13%.

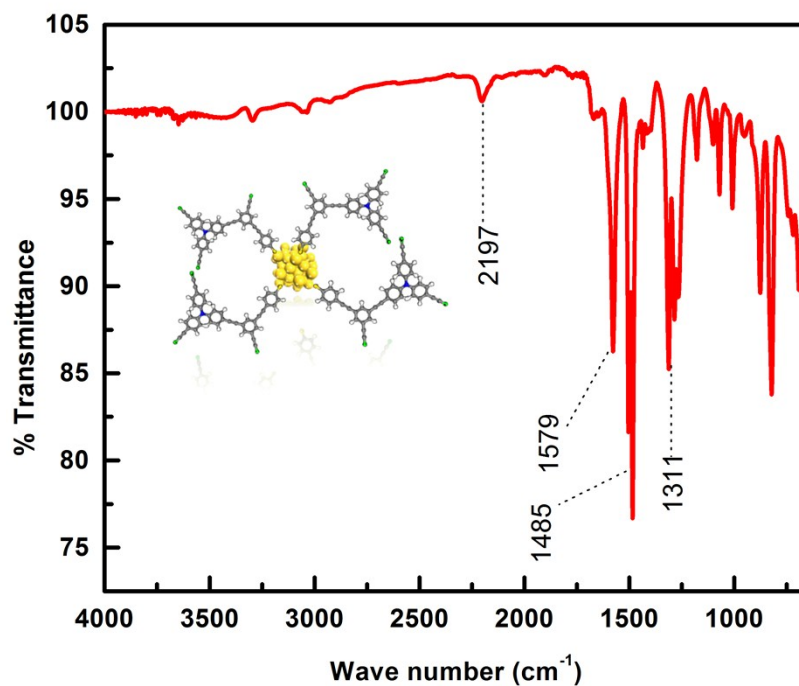


Figure S9. ATR-FTIR spectrum for 2.

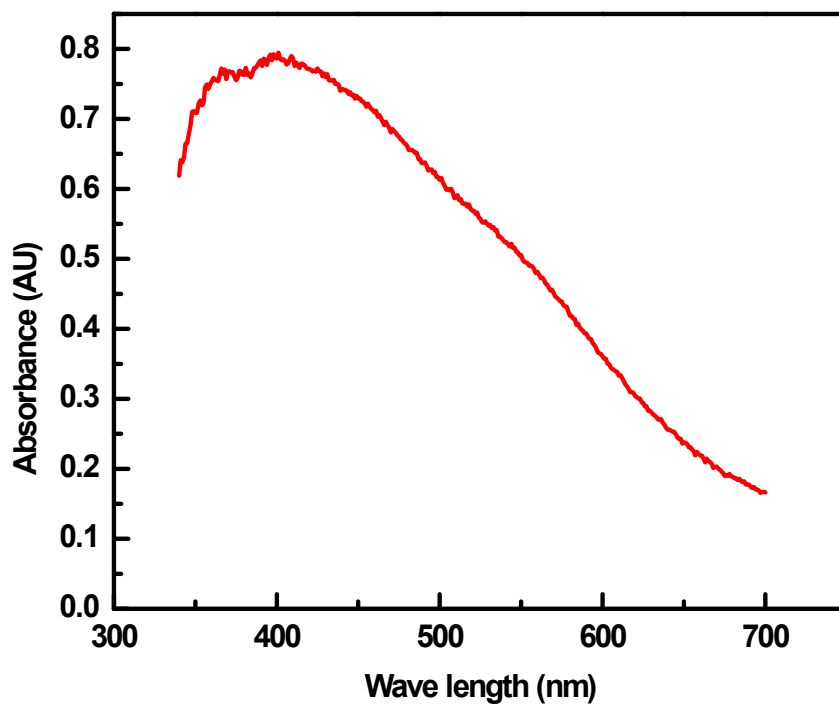


Figure S10. UV-Vis spectrum for 2.

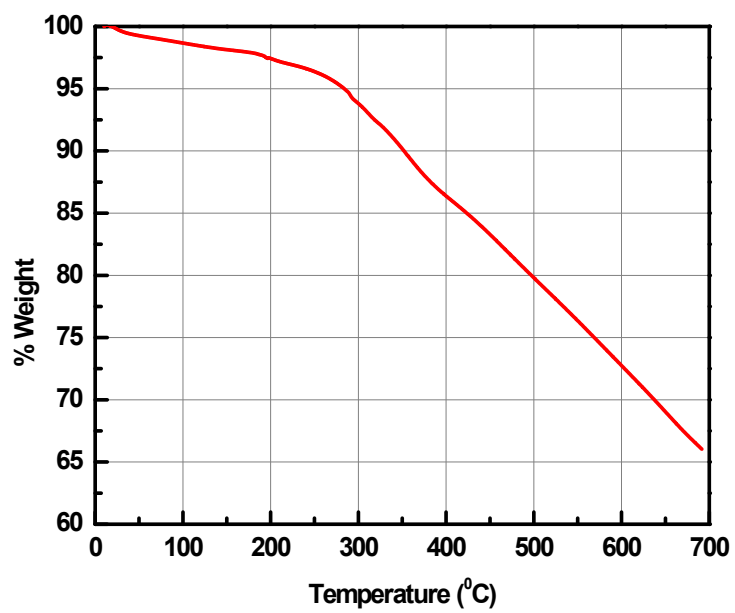
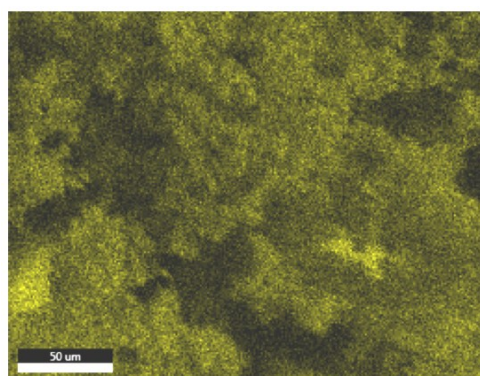
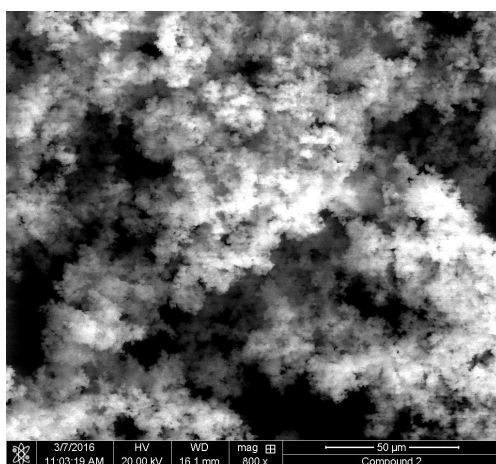
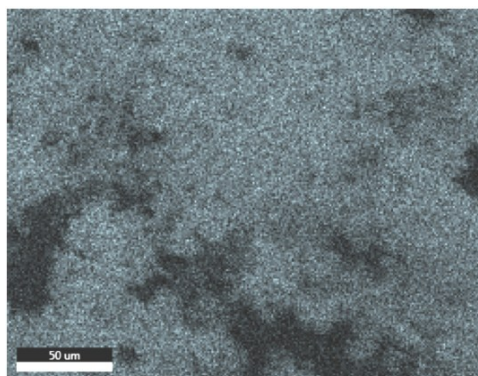


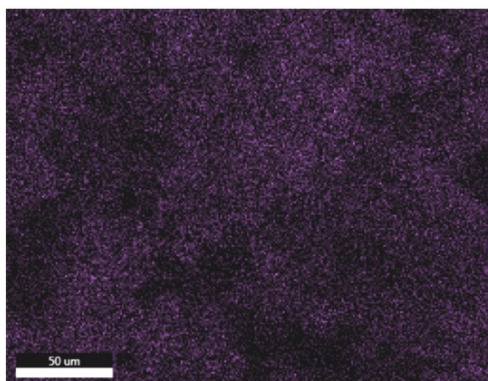
Figure S11.TGA analysis of 2.



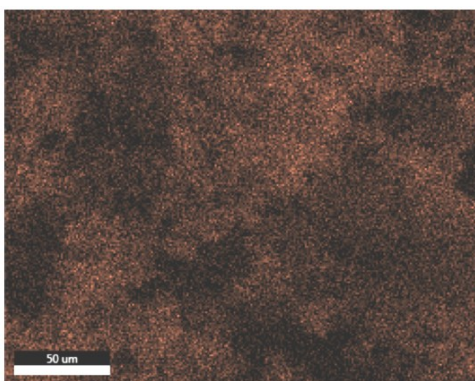
C K



BrL

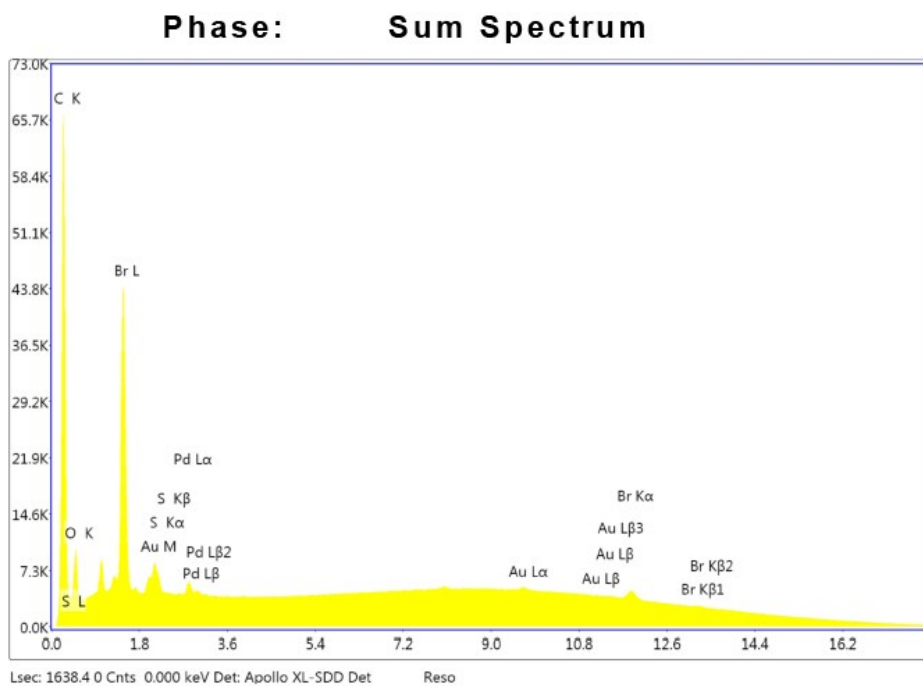


S K



AuL

Figure S 12: SEM image of **2** (top), and Energy-dispersive X-ray spectroscopy (EDX) maps showing the elemental distribution of C, Br, S, and Au.

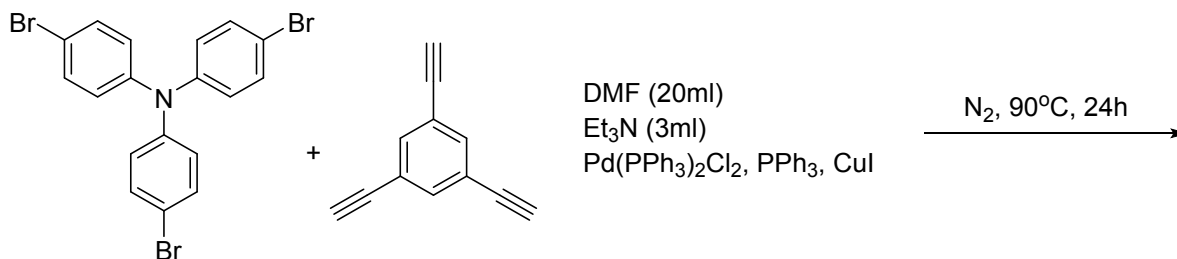


eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	67.58	80.67	354.3	0
O K	19.59	17.55	76.6	0
BrL	7.69	1.38	168.4	0
S K	0	0	0	1
PdL	0.37	0.05	6.2	0.1
AuL	4.76	0.35	8.3	0.16

Figure S13. EDX elemental analyses results for compound 2.

Synthesis of 2 without AuNPs



In a dry 100 ml pressure vessel, DMF (20 mL) and triethylamine (2 ml) were cooled in liquid nitrogen bath, degassed through three freeze-pump-thaw cycles and maintained under nitrogen atmosphere. To this prepared solution was added **tris(4-bromophenyl)amine** (0.12 mmol, 58.2mg), **1,3,5-triethynylbenzene** (0.12 mmol, 18 mg), Pd(PPh₃)₂Cl₂ (10 mg, 0.014mmol), PPh₃ (5 mg, 0.019 mmol) and CuI (5 mg, 0.026 mmol). The tube was then sealed with a Teflon screw under flow of nitrogen and the reaction mixture was then placed in an oil bath maintained at 90°C for 24 hr. The mixture was left to cool down to room temperature and the formed ppt was filtered under vacuum through a sintered glass funnel. The ppt was washed with DMF, MeOH and left to exchange in MeOH at 80°C overnight. The ppt was filtered again, washed with MeOH and left to exchange in MeOH at room temperature.

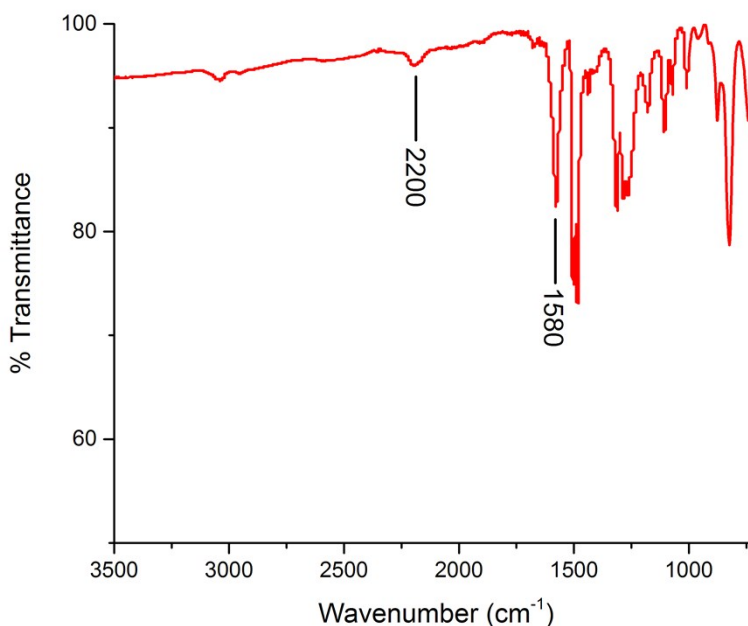


Figure S14. FT-IR spectrum for the solid isolated without added AuNPs

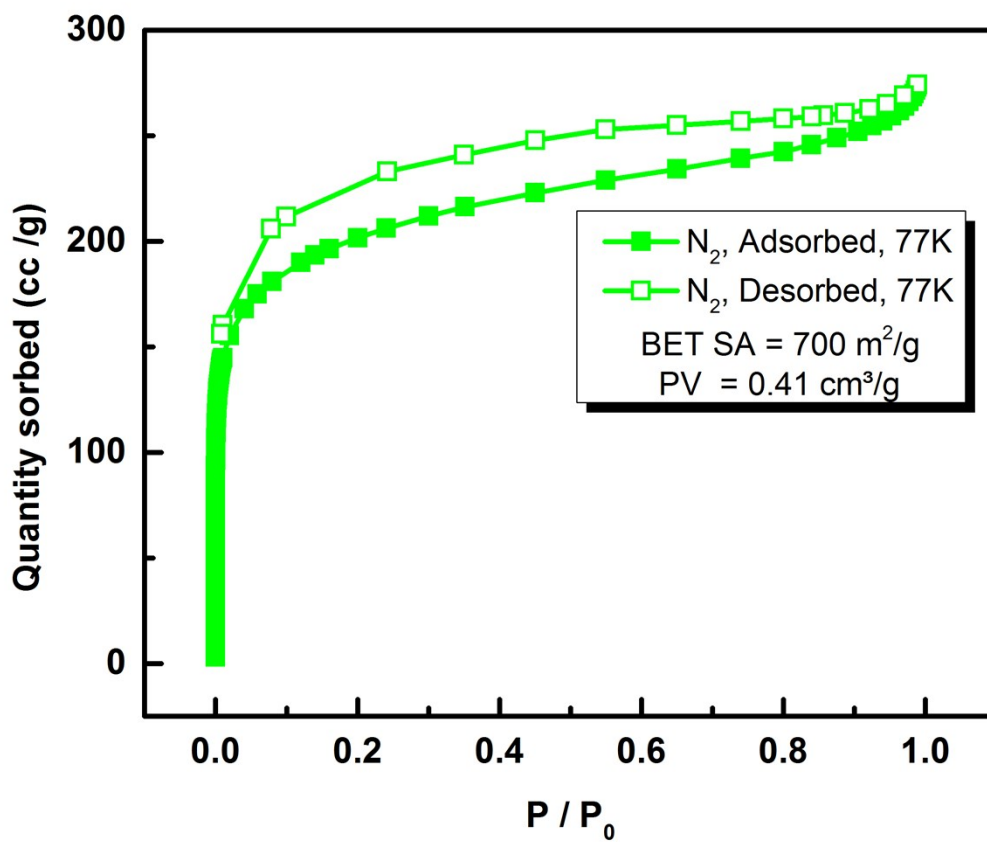


Figure S15. The N₂ adsorption/desorption isotherms for the polymer made with no AuNPs.

Synthesis 3:

In a similar way to synthesis of **2** but with using only a colloidal solution of citrate-capped gold nanoparticles (16 mL, 0.016 mmol Au) and 10 mL DMF solution of **4-bromothiophenol** (1.5 mg, 0.008 mmol) and the mixture was mixed thoroughly. The dry weight of the product was found to be 79 mg. Elemental Analysis: C, 70.37%; H, 3.278%; N, 3.429%; S, 0.097%.

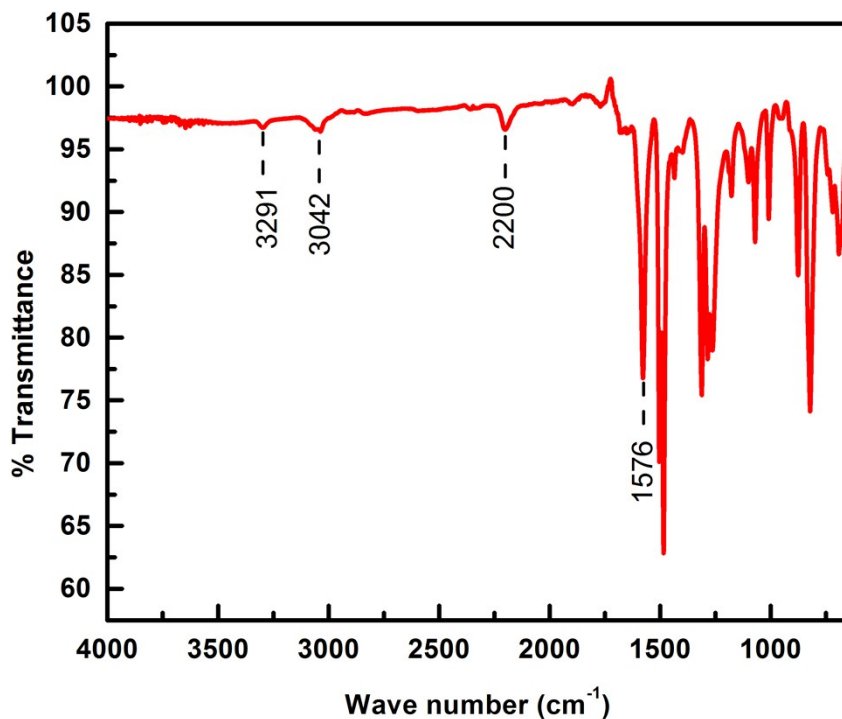


Figure S16. ATR-FTIR spectrum for **3**.

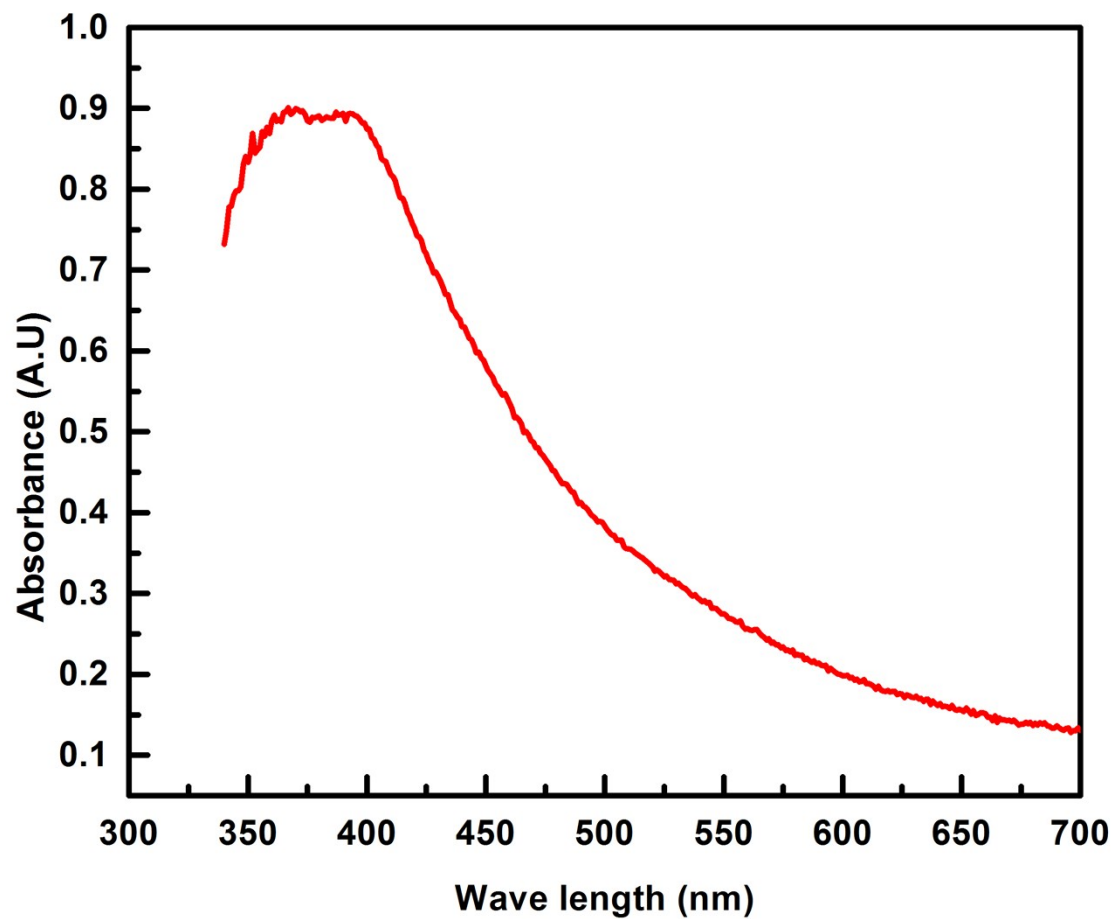


Figure S17. UV-Vis spectrum for 3.

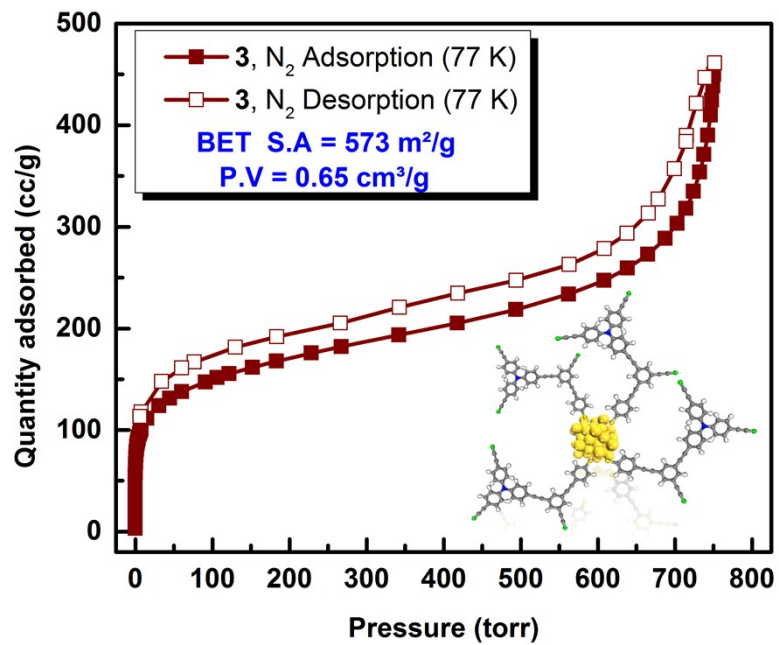
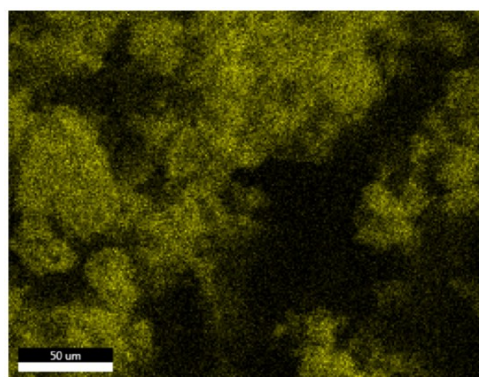
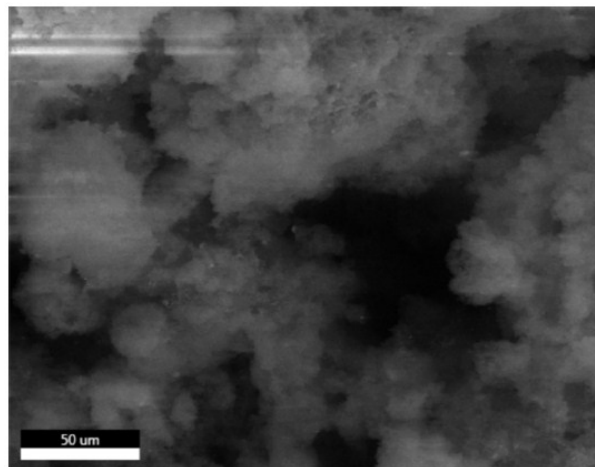
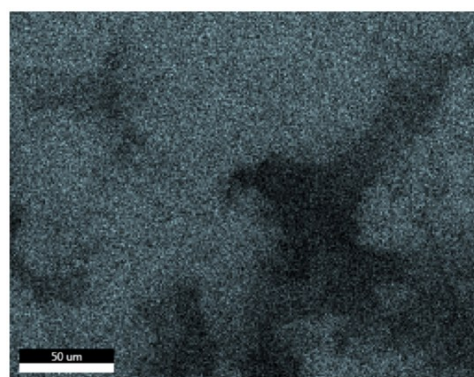


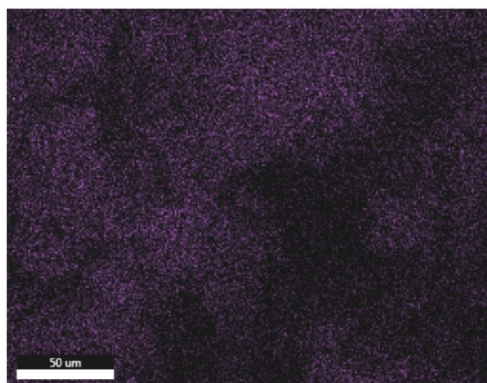
Figure S18: N₂ gas sorption isotherms in **3**.



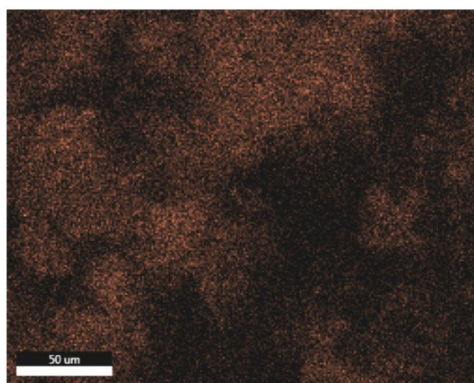
C K,



BrL

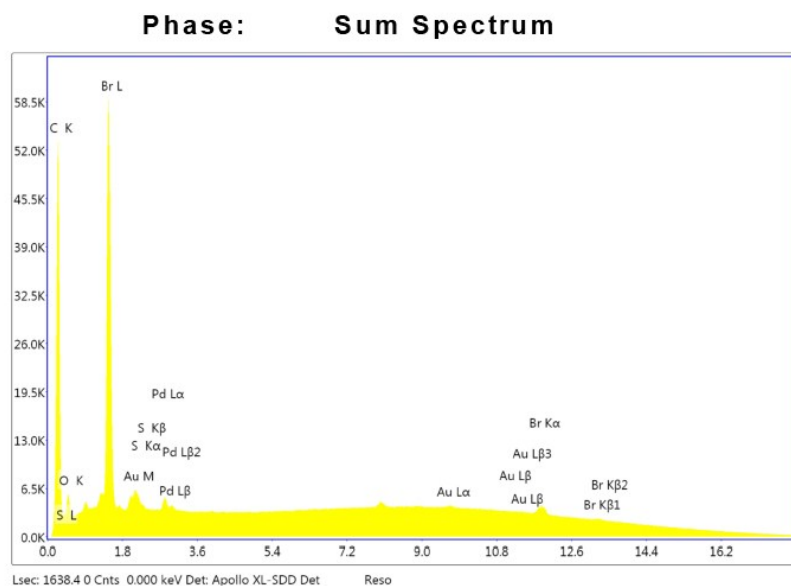


S K,



AuL

Figure S19: SEM image of **3** (top), and Energy-dispersive X-ray spectroscopy (EDX) maps showing the elemental distribution of C, Br, S, and Au.



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	69.71	84.11	282.1	0
O K	14.85	13.45	49.4	0
BrL	11.59	2.1	232.7	0
S K	0.04	0.02	1.1	0.53
PdL	0.59	0.08	8.8	0.04
AuL	3.23	0.24	5.3	0.12

Figure S20. EDX elemental analyses results for compound **3**

Synthesis of 4:

In a 100 mL round bottom flask a colloidal solution of citrate-capped gold nanoparticles (25 mL, 0.025 mmol Au) was added, followed by 10 mL DMF solution of **4-bromothiophenol** (2.67 mg, 0.014 mmol) and the mixture was mixed thoroughly. Most of the aqueous phase was removed under reduced pressure at 90°C in a rotary evaporator, the final mixture volume was 7 mL, and extra DMF was added to bring the final volume to 20mL. To this solution was added 2 mL of **triethylamine**. The solution was transferred to a 100 mL pressure vessel, cooled in liquid nitrogen bath, degassed through three freeze-pump-thaw cycles and maintained under nitrogen atmosphere. To this prepared solution was added tetrakis(4-bromophenyl)methane(63.6 mg, 0.1 mmol), **1,3,5-triethynylbenzene** (22 mg, 0.15 mmol), **CuI** (5 mg, 0.026 mmol), **Pph3** (5 mg, 0.019 mmol) and **PdCl₂(Pph₃)₂** (10 mg, 0.014 mmol) and the tube was sealed with a teflon screw under flow of nitrogen. The reaction mixture was then placed in an oil bath maintained at 90°C. After 24 h, a deep-brown precipitate formed, centrifuged in a 50 ml falcon tube at 8000 rpm for 30 seconds. The DMF supernatant was removed, and the precipitate washed with DMF and centrifuged again. Supernatant removal/centrifugation was repeated using DCM, then MeOH and kept under MeOH at room temperature for 3 days for guest exchange. The dry weight of the product was found to be 64 mg.

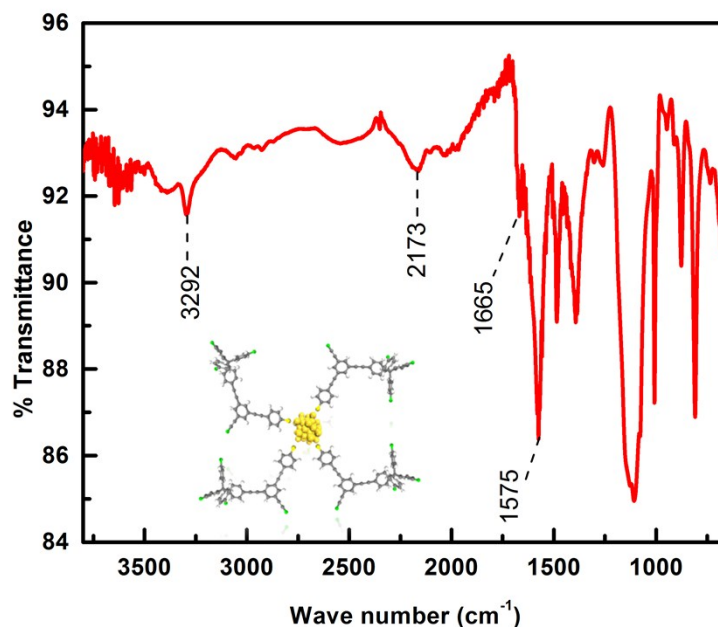


Figure S21: ATR-FTIR spectrum of 4.

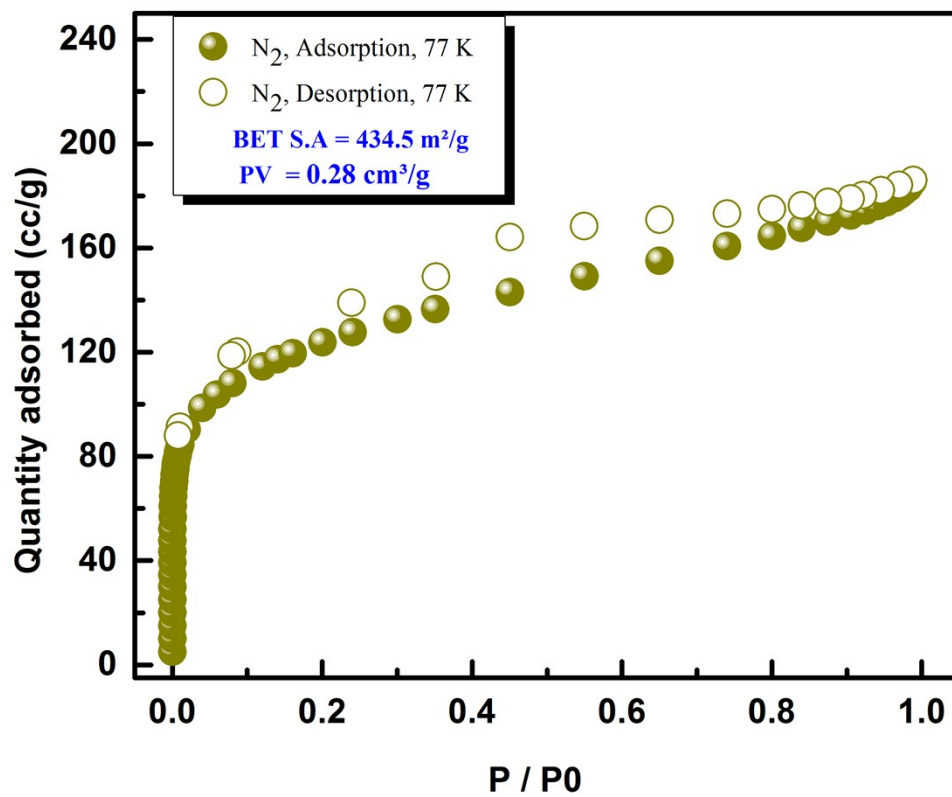
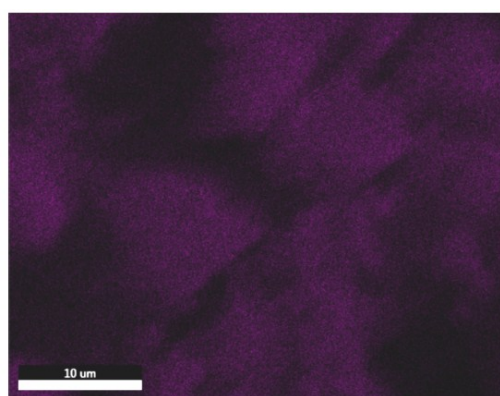
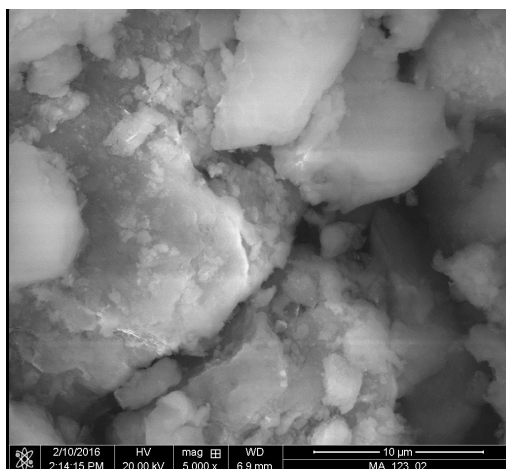
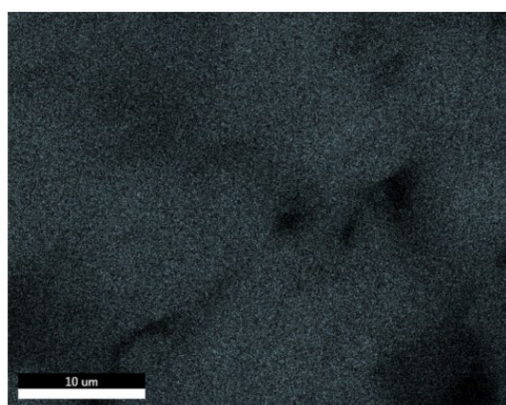


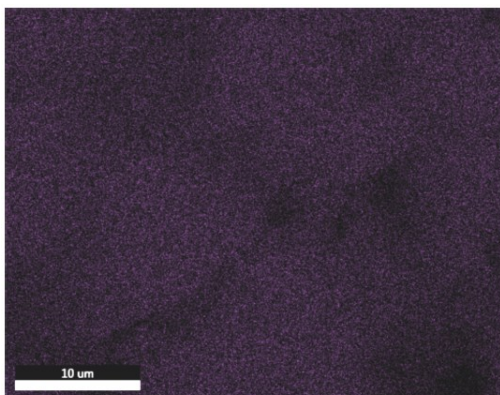
Figure S22: N₂ gas sorption isotherms in 4.



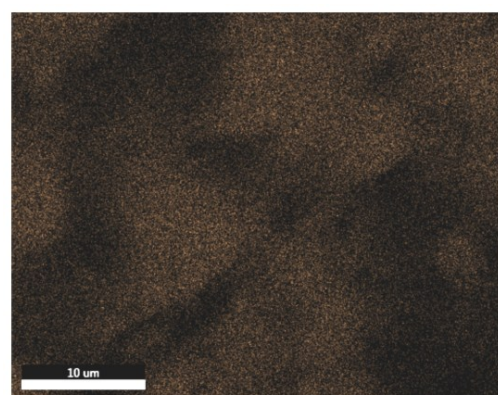
C K,



BrL



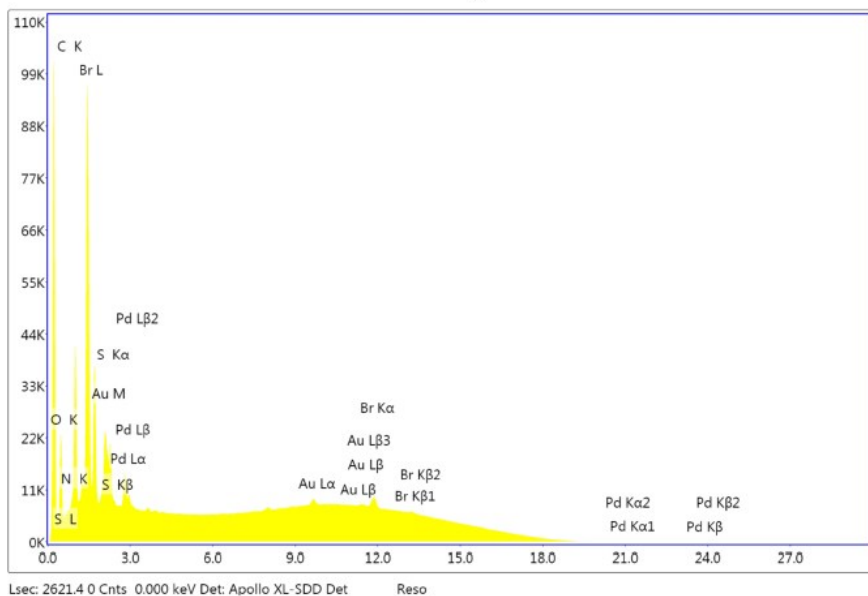
S K



AuL,

Figure S23: SEM image of **4** (top), and Energy-dispersive X-ray spectroscopy (EDX) maps showing the colour coded images for C, Br, S, Au.

Phase: Sum Spectrum



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	54.09	66.87	306.6	0
N K	12.68	13.44	17.9	0.01
O K	18.61	17.27	82.8	0
BrL	8.76	1.63	230.8	0
S K	0.73	0.34	32.3	0.01
PdL	0.96	0.13	19.3	0.02
AuL	4.17	0.31	9	0.15

Figure S24. EDX elemental analyses results for compound 4

Synthesis of 5:

In a similar procedure to that of 4 with the exception of using citrate-capped gold nanoparticles (16 mL, 0.016 mmol Au) and 10 ml DMF solution of **4-bromothiophenol** (1.5 mg, 0.008 mmol). The dry weight of the product was 45 mg.

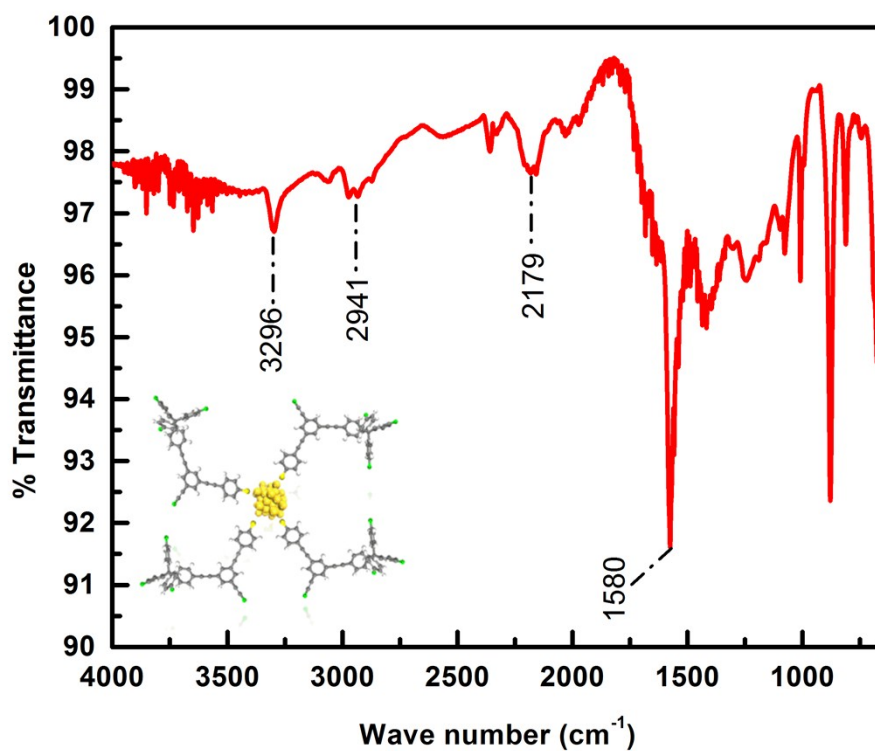


Figure S25: ATR-FTIR spectrum of 5.

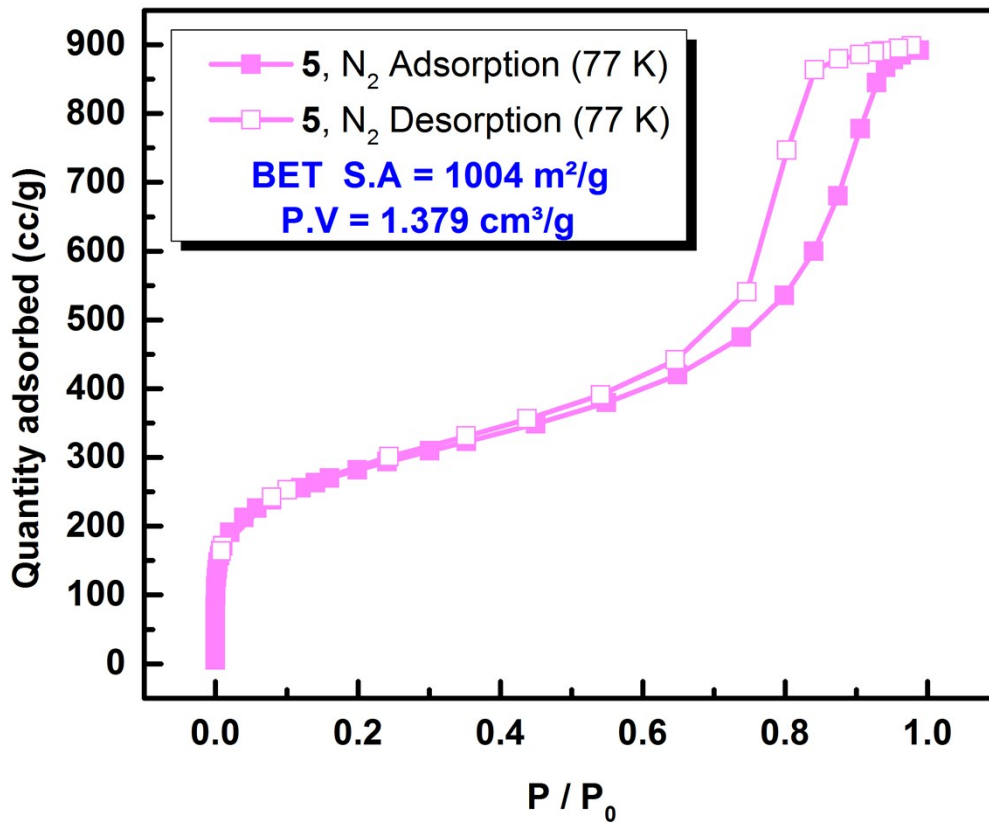
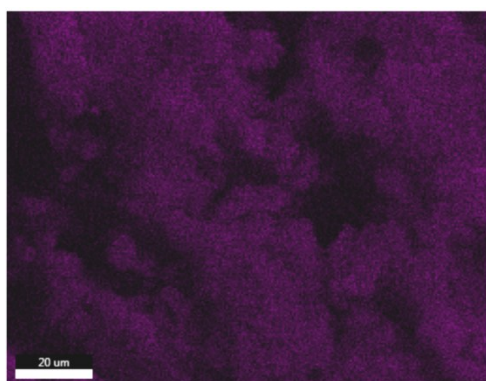
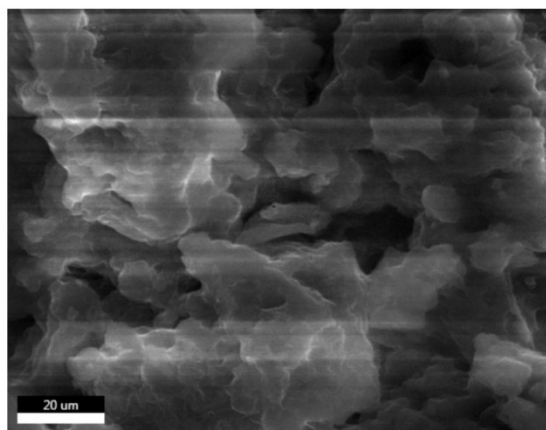
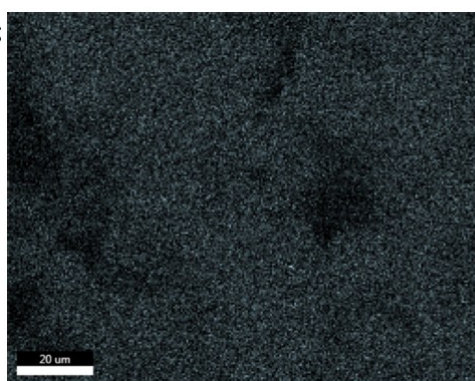


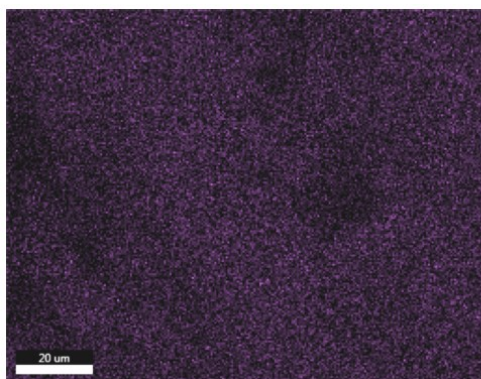
Figure S26: N₂ gas sorption isotherms in 5.



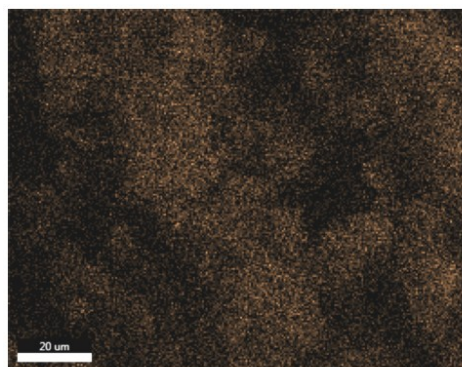
C K



Br L



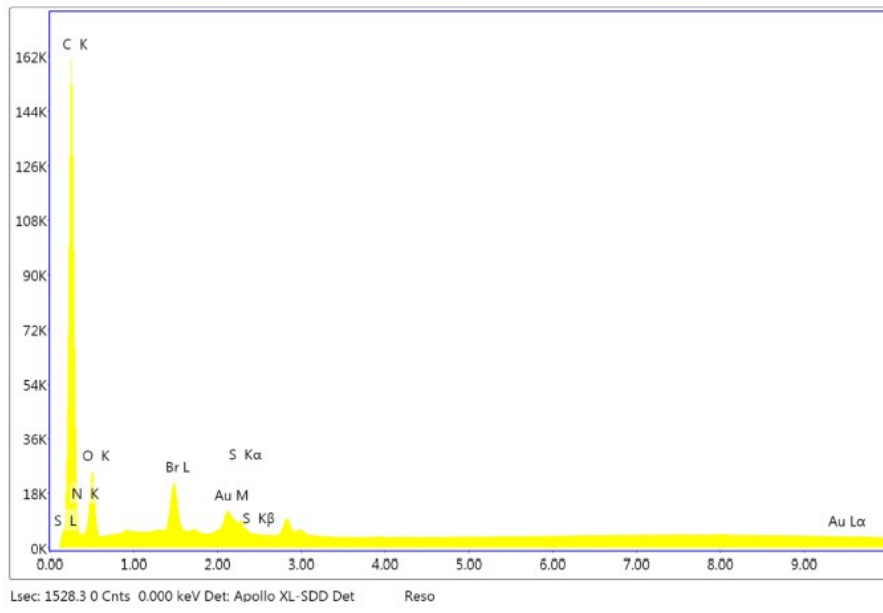
S K



Au L

Figure S27: SEM image of **5** (top), and Energy-dispersive X-ray spectroscopy (EDX) maps showing the elemental distribution of C, Br, S, and Au..

Phase: Sum Spectrum



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	64.59	72.78	804.9	0
N K	10.38	10.03	20.6	0.01
O K	19.31	16.33	131.4	0
BrL	2.68	0.45	69.6	0.01
AuM	2.5	0.17	41	0.02
S K	0.55	0.23	21.2	0.02

Figure S28. EDX elemental analyses results for compound 5