Supporting Information

Facile Synthesis of a Conjugated Microporous Polymeric Monolith via Copper-Free Sonogashira-Hagihara Cross-Coupling in Water Under Aerobic Conditions

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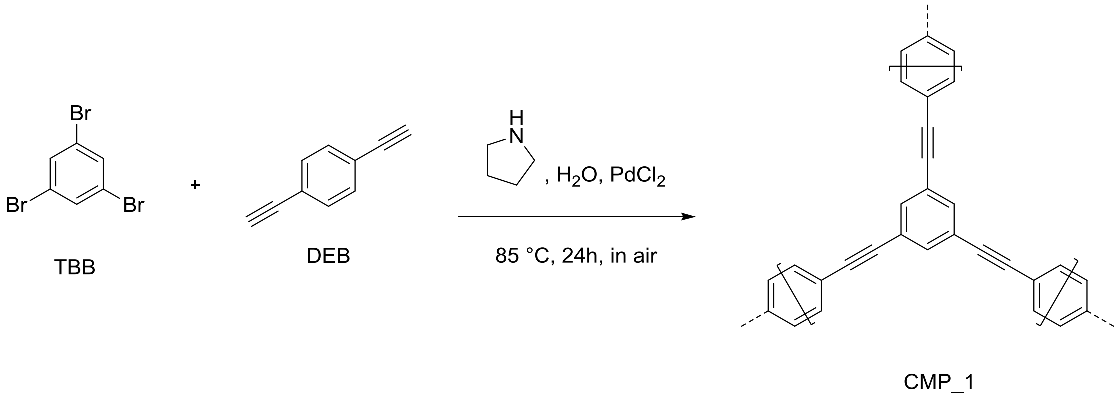
Physical Measurements

FT-IR spectra were measured using a Nicolet Avatar 360 FT-IR spectrophotometer. **FT-Raman** spectra were obtained using a FT-IR, NIR-FT-Raman Perkin–Elmer Spectrum 2000 instrument equipped with a diode pumped Nd:YAG laser PSU and using the standard Spectrum v2.0 software. **Solution ^{1}H NMR** spectra were recorded on a 400 MHz Bruker superconducting-magnet high-field NMR spectrometer at room temperature, with tetramethylsilane (TMS) as the internal standard. **Thermogravimetric analyses** (TGA) were carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (STA 6000) with a heating rate of 5 °C/min, with an empty Al_2O_3 crucible being used as the reference. **Porosity and surface area analysis** was performed using a Quantachrome Autosorb iQ gas sorption analyzer. Each sample was outgassed at 0.03 torr with a 2 °C/min ramp to 100 °C and held at 100 °C for 12 hours. The sample was then held at vacuum until the analysis was run. Pore analysis was performed using CO_2 at 273 K (P range of 8×10^{-3} to 780 mmHg). The amounts of the metal ions were determined by using a PerkinElmer Optima™ 2100 DV **ICP optical emission spectrometer**. **Scanning Electron Microscope** (SEM) was carried out on Philips XL30 Esem-FEG, (FEI Company, the Netherlands) equipped with an **energy-dispersive x-ray microanalysis** (EDX) system (EDAX Phoenix system, EDAX Inc., Mahwah NJ, USA). **Solid State ^{13}C {1H} CP-MAS** measurements were carried out using a Bruker Avance 400 spectrometer operating at 100.6 MHz for 13C using a Bruker 4 mm double resonance probe-head operating at a spinning rate of 10 kHz.

Experimental section

Staring materials, reagents and solvents were purchased from commercial sources (pyrrolidine from Merck, palladium chloride from J&K and the others from Aldrich) and used without further purification.



Scheme 1. Synthetic scheme for the CMP monolith (CMP_1).

Synthesis of the monolithic polymer (CMP_1). 1,3,5-Tribromobenzene (157.5 mg, 0.50 mmol), 1,4-diethynylbenzene (95.0 mg, 0.75 mmol) and $PdCl_2$ (1.25 mg, 0.007 mmol) were dissolved in pyrrolidine (2.0 mL) with the aid of a sonication bath in a 7.5-mL sintering vial to get a clear dark brown solution. DI water (3.0 mL) was then added (a large amount of precipitate was formed), and then the mixture was sonicated for about 2 minutes. The reaction mixture was heated at 85 °C in a heating block for 24 hours, and a deep brown monolithic solid was formed. The monolith was washed with DI water and methanol for several times.

Purification of the monolithic CMP_1. A thimble (e.g., made from folding filter paper) containing the monolithic polymer sample was loaded into the main chamber of a Soxhlet extractor. The Soxhlet extractor was connected onto a 250-mL round bottom flask containing methanol (150 mL), and then equipped with a condenser. The solvent is heated at 100 °C by an oil bath for 6 hours. Afterwards similar steps of extraction--lasting also 6 hours--were conducted by using tetrahydrofuran (150 mL) and acetone (150 mL) in lieu of the methanol. The filter paper was then taken out and the solid was dried in vacuum to give the purified monolithic CMP sample (97 mg, yield: 73.5%).

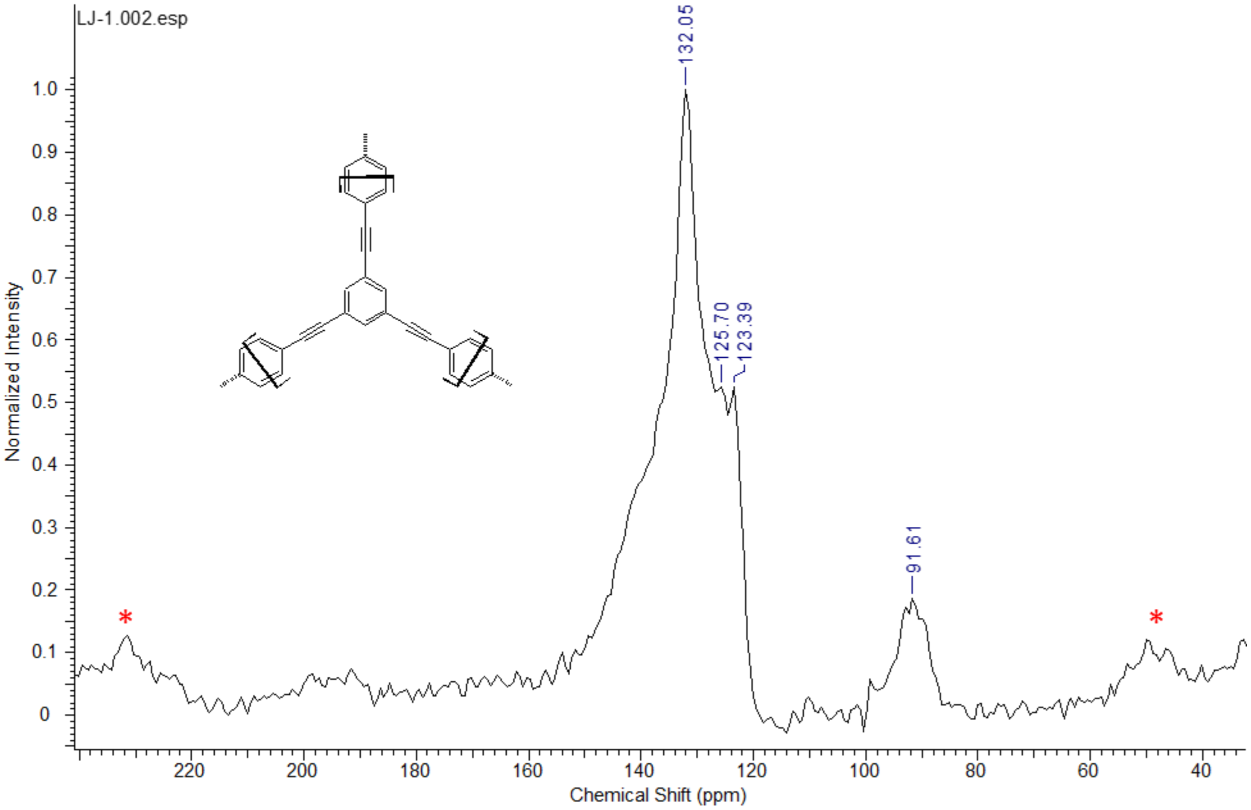


Figure S1. Solid state ^{13}C-NMR analysis of the monolithic CMP_1. Aromatic carbons can be seen in the δ 123-132 region while the alkyne peak can be seen at δ 91.61. Peaks denoted by (*) indicate the presence of side bands.

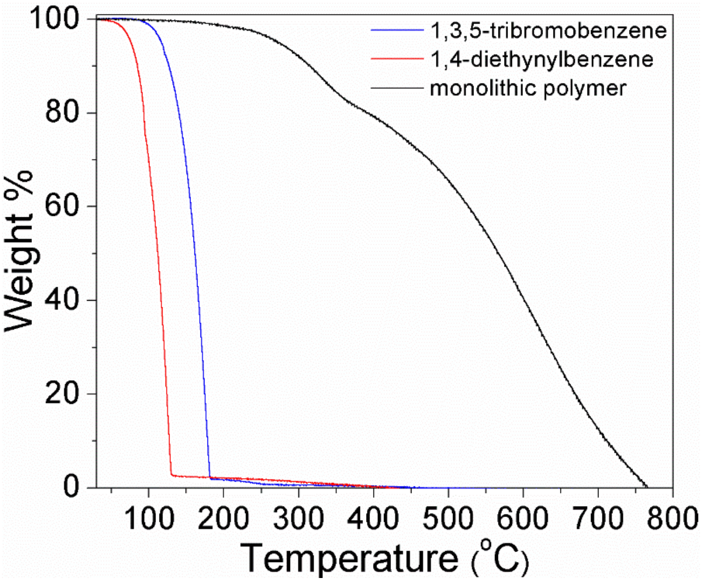


Figure S2. Thermogravimetric analysis (TGA) plots of 1,3,5-tribromobenzene (blue line), 1,4-diethynylbenzene (red line) and monolithic CMP_1 (black line).

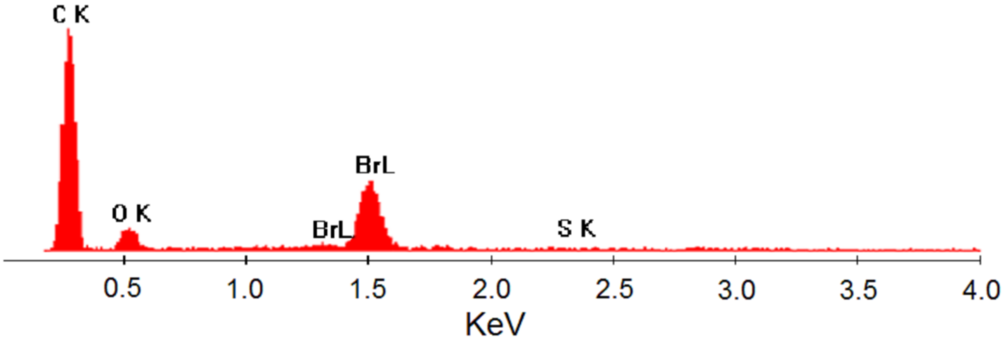


Figure S3. An energy-dispersive X-ray (EDX) spectrum of monolithic CMP_1 sample.

Gas sorption. Pore analysis of the activated monolithic polymer sample was performed using CO_2 at 273 K (P range of 8×10^{-3} to 780 mmHg). Initial data analysis was done using the AS1Win and QuadraWin 5.05 software (both of Quantachrome instruments). NLDFT analysis (Pore Size Distribution and Pore Volume, Figure S4) of the CO_2 adsorption isotherm (273 K) was done using a commercialized model (CO_2 at 273 K on carbon; NLDFT model). The PSD and pore volume of CO_2 showed us an average pore width of 0.48 nm and a micropore volume of 0.113 cm^3/g.

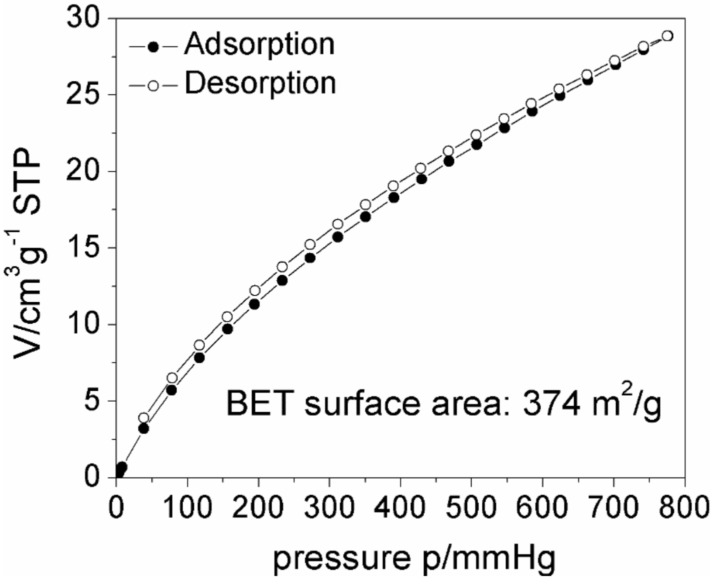


Figure S4. CO_2 sorption isotherm at 273 K for the monolithic CMP_1 (113.4 mg, activated by evacuating at 100 °C for 12 hours).

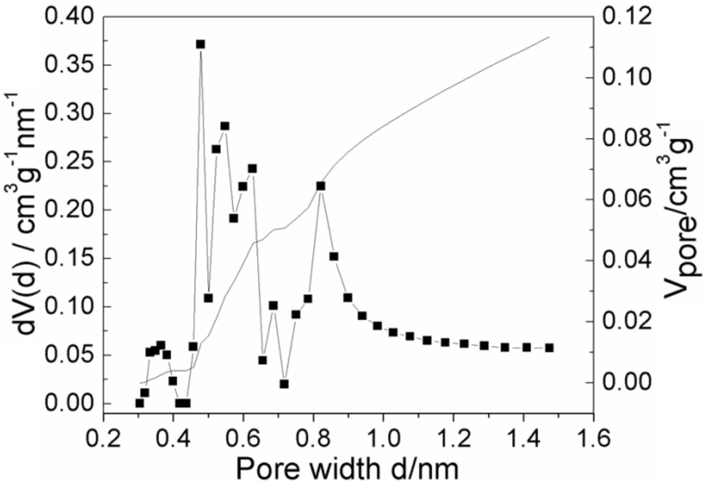


Figure S5. Pore size distribution and Pore volume of the monolithic CMP_1 (CO_2 gas at 273 K; NLDFT model).

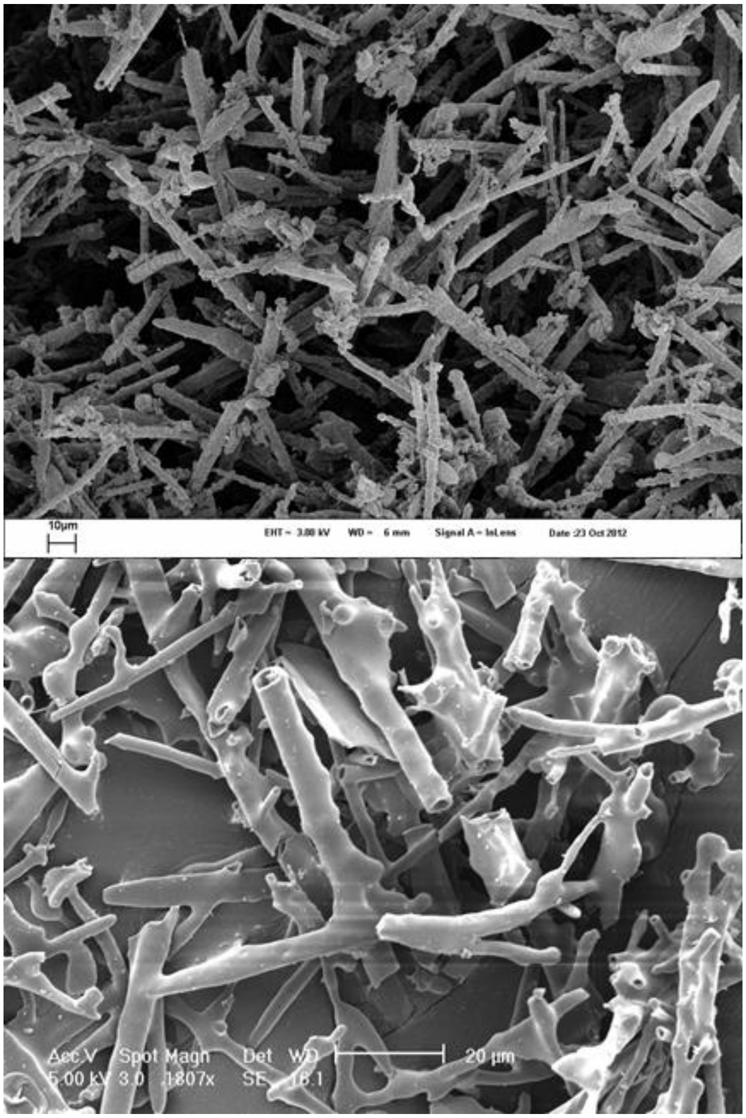
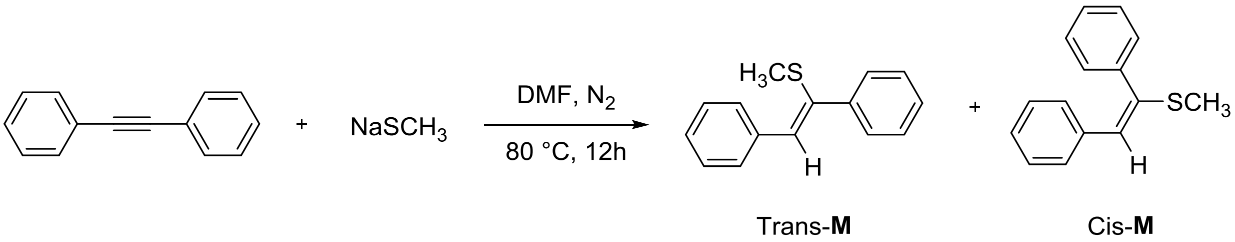
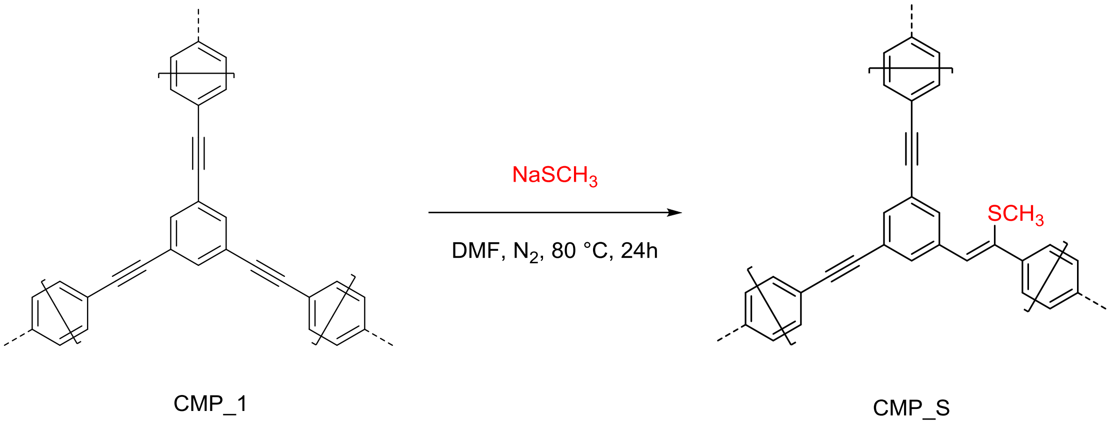


Figure S6. SEM imaging reveals that CMP_1 is primarily composed of hollow fibres with diameters in the range of a few hundred of nanometers.



Scheme S1. Synthesis of homogeneous M molecule using a thiol-yne reaction.

Diphenylacetylene (100 mg, 0.56 mmol) and $NaSCH_3$ (94 mg, 1.34 mmol) were added into a 10-mL, two-neck, round-bottom flask equipped with a magnetic stirring bar. Dimethylformamide (5 mL), previously deaerated by N_2, was then transferred into the round-bottom flask. The flask was placed in an oil-bath, stirred and heated at 80 °C for 12 hours. Upon cooling to room temperature, 1% HCl was then slowly added into the reaction mixture with vigorous stirring. After the pH value of the mixture was lower than 2, the mixture was poured into DI water (15 mL) and extracted by ethyl acetate (2x10 mL). The combined organic layer was then washed by DI water (3x10 mL), dried over $MgSO_4$, evaporated *in vacuo*. The crude product (yellow oil) was further purified by a silica gel column (with CH_2Cl_2/hexane 1:10 as the eluent) to provide light yellow oil (118.4 mg, 0.26 mmol, yield: 93.2%). ^{1}H NMR (400 MHz, $CDCl_3$) *trans*-**M** δ 7.07-7.69 (m, 10H, aromatic), 6.77 (s, 1H, =CH), 1.98 (s, 3H, SCH_3); ^{1}H NMR (400 MHz, $CDCl_3$) *cis*-**M** δ 6.91-7.69 (m, 10H, aromatic) 6.51 (s, 1H, =CH), 2.25 (s, 3H, SCH_3).



Scheme 2. Post-modification of the CMP_1 monolith using a thiol-yne reaction.

Typical conditions for modification of the monolithic CMP_1 by $NaSCH_3$. The polymer (repeat unit~261.3 g/mol, 65 mg, ~ 0.75 mmol of alkyne) and $NaSCH_3$ (126 mg, 1.8 mmol) were added into a 25-mL, two-neck, round-bottom flask equipped with a magnetic stirring bar. Dimethylformamide (10 mL), previously degassed by N_2, was then transferred into the round-bottom flask. The flask was placed in an oil-bath, stirred and heated at 80 °C for 24 hours. Upon cooling to room temperature, 1 % HCl was then slowly added into the reaction mixture with vigorous stirring. After the pH value of the mixture was lower than 2, the brownish-red solid was collected by suction filtration and washed with water (until pH=7), methanol (2x10 mL) and dichloromethane (2x10 mL). The CMP_S monolith was then dried under vacuum at room temperature for 24 hours.

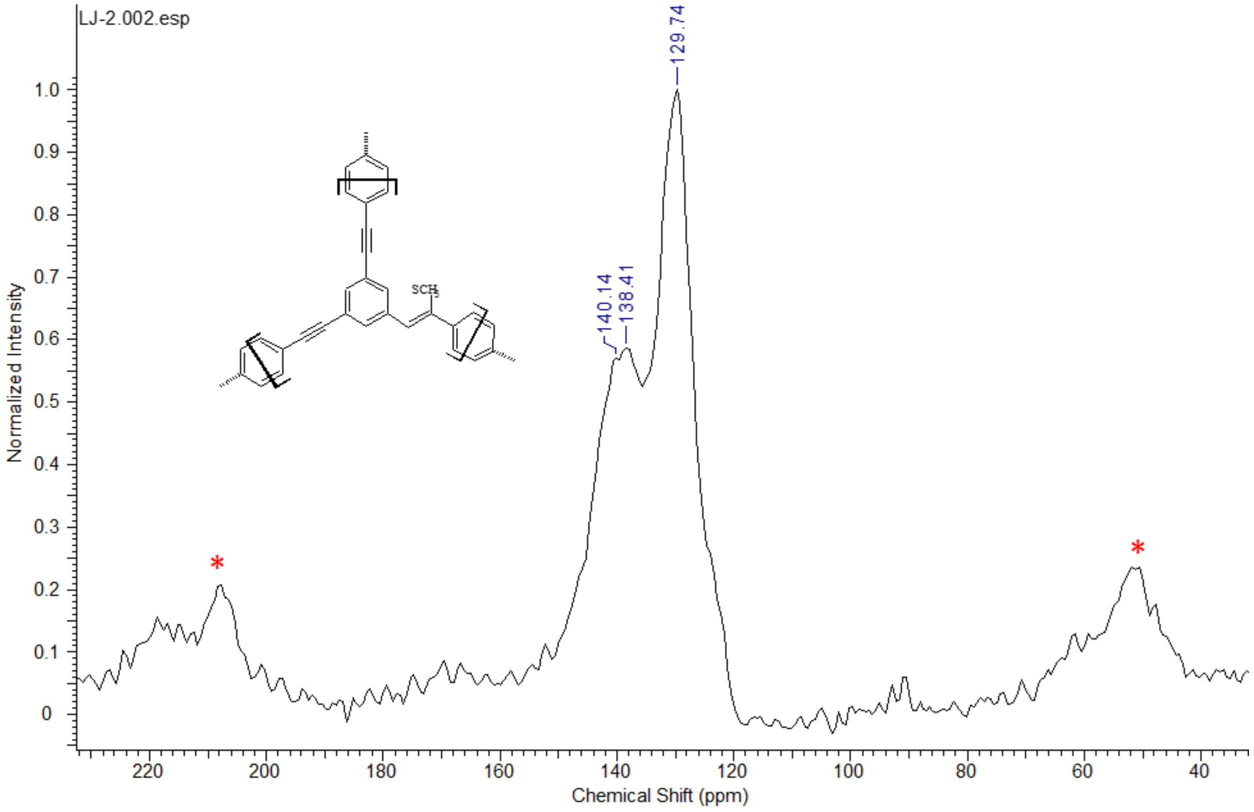


Figure S7. Solid state ^{13}C-NMR analysis of the monolithic CMP_S. Aromatic carbons can be seen in the δ 129-140 region while the alkyne peak has receded. Peaks denoted by (*) indicate the presence of side bands.

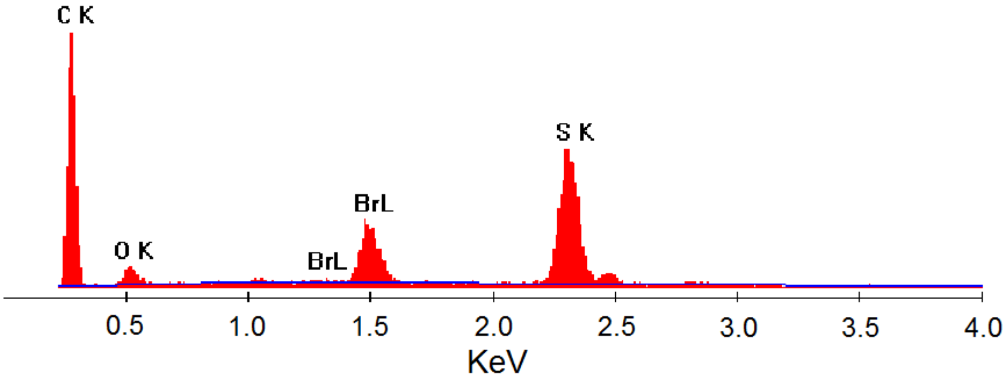


Figure S8. An energy-dispersive X-ray (EDX) spectrum of CMP_S sample.

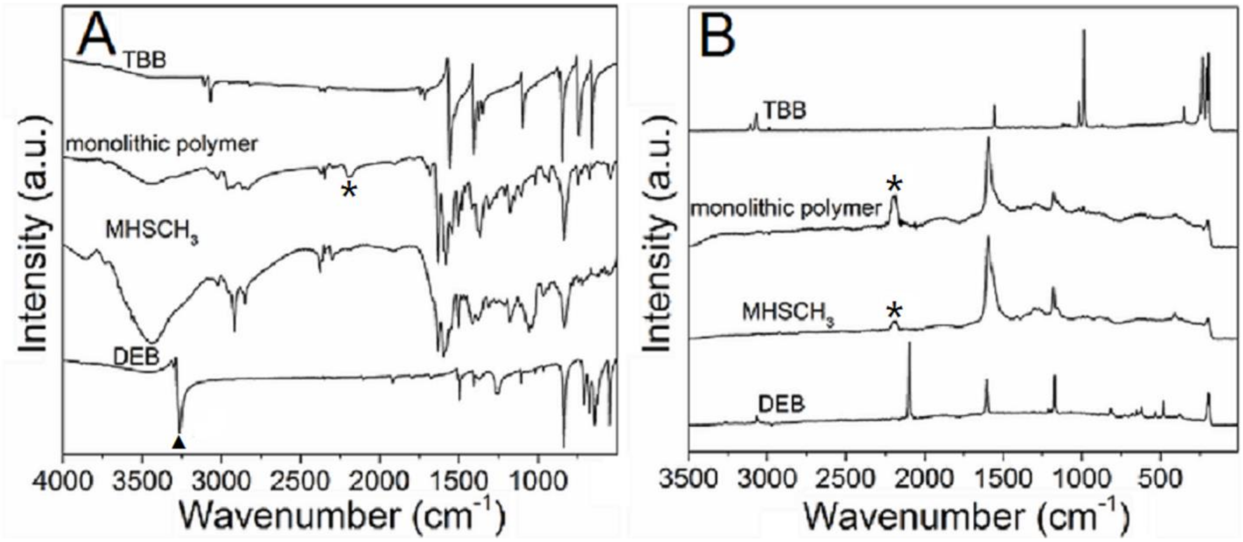


Figure S9. The IR (A) and Raman (B) spectra of 1,3,5-tribromobenzene (TBB), monolithic CMP_1, CMP_S and 1,4-diethynylbenzene (DEB). (▲: C-H stretching mode of terminal alkynes; stars: typical C≡C stretching mode).

Ag^I uptake by CMP_S. To probe the upper limit of Ag^I uptake, the CMP_S solid (40 mg, 0.16 mmol of the desired repeat unit.) was placed in an aqueous solution containing excess $AgNO_3$ (156 mg , 0.92 mmol) in 3 mL DI water. After the mixture was stirred for 1 day at 80 °C in the dark (with the vial wrapped by aluminum foil), the resultant solid was separated by filtration and washed repeatedly by DI water (5x10 mL) to remove residual unbound Ag^I species and dried under vacuum for overnight. Ag^I content of the $AgNO_3$ treated sample was then measured by ICP, which indicated that Ag content to be 8.75%.

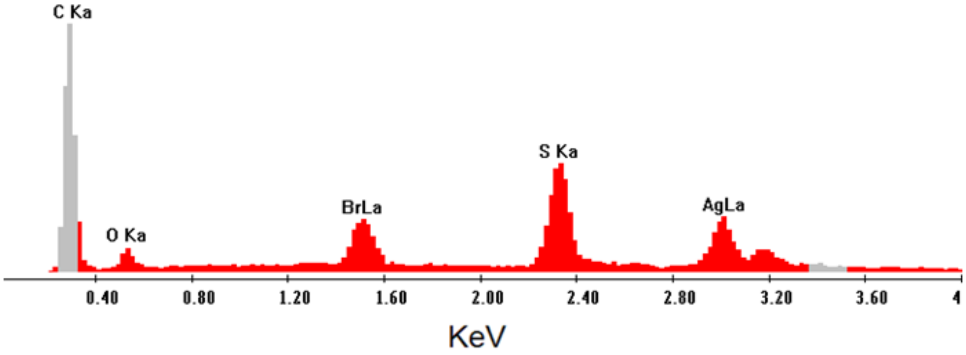


Figure S10. An energy-dispersive X-ray (EDX) spectrum of CMP_S_Ag sample.

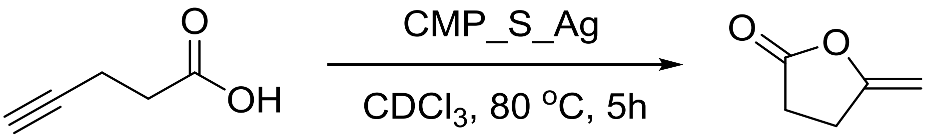
Selective Ag^I uptake. Monolithic CMP_1 (10 mg, 0.04 mmol of the repeating unit) and CMP_S (10 mg, 0.03 mmol of the repeating unit) were separately added into two aqueous solutions (each was 10 mL) of a mixture of $AgNO_3$, $Pb(NO_3)_2$, $Cd(NO_3)_2{\cdot}4H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}2H_2O$, with the concentration each metal ion being set at about 10 ppm (see Table S1 and S2 for the specific figures). The mixtures were then stirred in the dark and small portions of the solution was taken out at different times (0h, 2h and 20 h) for determining the concentrations of the remaining metal species.

Table S1. The concentrations (ppm) of the individual metal ions in a mixture solution at different hours after being mixed with monolithic CMP_1.

ions time	Pb^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Co^{2+}	Ag^{+}
0 h	8.14	10.9	9.18	9.56	10.0	9.46	9.23
2 h	6.08	10.9	8.11	9.50	9.92	9.45	4.81
20 h	6.57	10.7	8.55	9.59	9.88	9.50	4.84

Table S2. The concentrations (ppm) of the individual metal ions in a mixture solution at different hours after being mixed with the monolithic CMP_S.

ions / time	Pb^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Co^{2+}	Ag^{+}
0 h	8.14	10.9	9.18	9.56	10.0	9.46	9.23
2 h	5.44	10.8	7.99	9.48	9.97	9.50	1.48
20 h	3.90	10.7	6.84	9.46	9.76	9.47	0.57



Scheme 3. CMP_S_Ag mediated cyclisation of 4-pentynoic acid.

Typical conditions for heterogeneous catalytic reactions (Synthesis of 5-methylenedihydrofuran-2(3H)-one) by $AgNO_3$ treated CMP_S (CMP_S_Ag). 4-Pentynoic acid (10 mg, 0.10 mmol) was dissolved in $CDCl_3$ (0.5 mL) in a 3.5-mL glass vial equipped with a magnetic stirring bar. CMP_S_Ag (6.2 mg, Ag/substrate molar ratio: 5%) was added into the mixture, the reaction mixture was then heated at 80 °C in a heating block with stirring. After 5 hours, the clear solution (obtained by centrifugation of the reaction mixture) was directly analyzed by ^1H NMR. The solid (catalyst) was used for at least another 4 cycles after washing by $CHCl_3$ and drying under vacuum. ^1H NMR

(400 MHz, $CDCl_3$) δ 4.75 (s, 1H, =CH), 4.31 (s, 1H, =CH), 2.86-2.90 (t, 2H, CH), 2.65-2.67 (t, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.09, 155.83, 88.94, 28.19, 25.27.

Catalytic activity test of the reaction supernatant. After the catalytic reaction was completed (monitored by ^1H NMR), the catalyst was removed by simple filtration. The supernatant was collected and a new batch of reactant (4-pentynoic acid) was added to the supernatant. 0.1 mL of this solution was added to 0.5 mL $CDCl_3$ for ^1H NMR measurement. The remaining solution was heated at 80°C for 5 hours. The mixture was cooled to room temperature and 0.1 mL of this solution was taken out and added to another 0.5 mL $CDCl_3$ for ^1H NMR measurement. The ratio between 5-methylenedihydrofuran-2(3H)-one and 4-pentynoic acid was unchanged after heating at 80°C for 5 hours, suggesting no catalytic activity for the isolated supernatant.

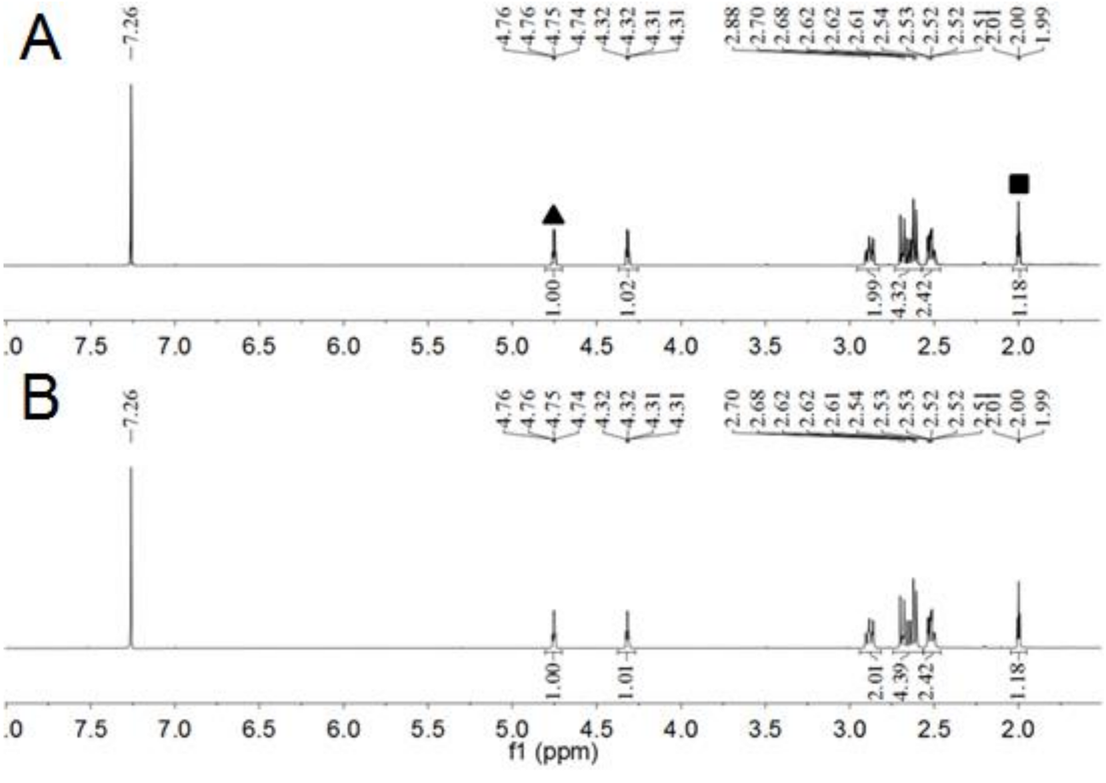


Figure S11. Solution ^{1}H NMR spectra of the reaction supernatant (a) before and (b) after stirring at 80°C for 5 hours. Characteristic peak labelling: ▲, 5-methylenedihydrofuran-2(3H)-one; ■, 4-pentynoic acid.

Typical condition for heterogeneous catalytic reaction of 4-pentynoic acid by $AgNO_3$ salt. 4-Pentynoic acid (10 mg, 0.10 mmol) was dissolved in $CDCl_3$ (0.5 mL) in a 3.5-mL glass vial equipped with a magnetic stirring bar. $AgNO_3$ salt (0.85 mg, Ag/substrate molar ratio: 5%) was added into the mixture, the reaction mixture was then heated at 80 °C in a heating block with stirring. After overnight reaction, the clear solution (obtained by centrifugation of the reaction mixture) was directly analyzed by ^{1}H NMR.

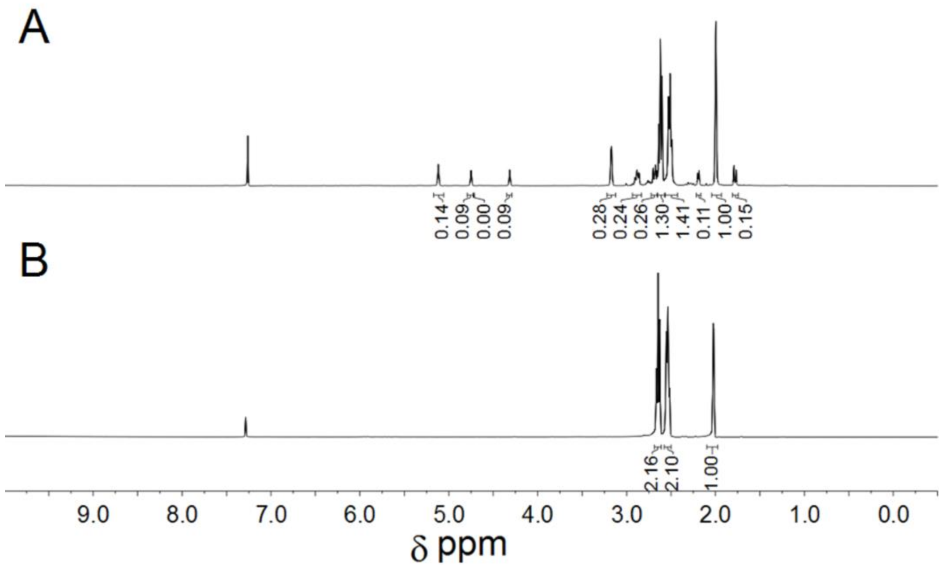


Figure S12. ^{1}H NMR of 4-pentynoic acid (B) and the clear reaction solution (A) after being stirried with $AgNO_3$ salt overnight.