

## Supporting Information:

# Carbon Black Functionalized with Hyperbranched Polymers: Synthesis, Characterization, and Application in Reversible CO<sub>2</sub> Capture

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## EXPERIMENTAL SECTION

**Materials.** Carbon black (Monarch 700) was supplied by Cabot Corp. (Billerica, MA). Sodium azide ( $\geq 99.5\%$ ), phosphorus tribromide ( $\text{PBr}_3$ , 99%), trimethylamine solution (31-35 wt. % in ethanol,  $\sim 4.2$  M), triethylamine ( $\geq 99\%$ ), thionyl chloride ( $\text{SOCl}_2$ ,  $\geq 99\%$ ), *N*-methyl-2-pyrrolidinone (NMP, 99%), *N,N*-dimethyl formamide (DMF) and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, 99%) were purchased from Aldrich and used as received. Styrene (St, 99%), *p*-Chloromethylstyrene (CMS,  $\geq 90\%$ ) and divinylbenzene (DVB, 80%) were purchased from Aldrich and purified by passing over a column of basic alumina to remove the inhibitor.  $\text{CuBr}$ ,  $\text{CuBr}_2$ ,  $\text{CuCl}$  and  $\text{CuCl}_2$  were purchased from Aldrich in the highest available purity. Potassium hydroxide ( $\text{KOH}$ ,  $\geq 85.0\%$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ , 99.9%), and nitric acid (69.5%) were purchased from Fisher Scientific and used as received. 2-Hydroxyethyl 2-bromoisobutyrate (HEBiB) was prepared as previously reported in literature.<sup>1</sup> Excellion membrane I-200 (SnowPure LLC, CA) was exchanged to the hydroxide form according to the procedures described elsewhere.<sup>2-4</sup>

**Instrumentation.** Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) measurements were performed on a Bruker Avance 300 MHz spectrometer. Thermogravimetric analysis (TGA) was obtained on a TG/DTA6300 analyzer (Seiko Instruments, Inc.) under  $\text{N}_2$  atmosphere (flow rate 50 mL/min). Elemental analyses were performed on an Exeter Analytical CE440 elemental analyser. Scanning electron microscopy (SEM) analysis was conducted using a Hitachi 2460N scanning electron microscope. The specimens were attached to SEM stubs using rubber cement or double sided sticky tape, and coated with gold using a Pelco SC-6 sputter coater. Digital images were obtained using Quartz PCI Image management system software. Transmission electron microscopy (TEM) analysis was conducted using a Hitachi H-7100 transmission electron microscope (Hitachi High Technologies America) operating at 75 kV. A small drop of solution containing the sample was placed on a carbon or formvar coated copper grid. After several seconds, the drop was allowed to evaporate or was removed by blotting with filter paper. The sample that remained on the grid was allowed to dry before inserting the grid into the microscope. Digital images were obtained using AMT Advantage 10 CCD Camera System

and NIH Image software. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet Avatar 360 FTIR spectrometer. Molecular weight and molecular weight distribution ( $M_w/M_n$ ) values were determined by gel permeation chromatography (GPC). The GPC was performed with a Waters 515 HPLC pump and a Waters 2414 refractive index detector using PSS columns (Styrogel 10<sup>2</sup>, 10<sup>3</sup>, 10<sup>5</sup> Å) in tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min at 35 °C. Absolute molecular weights ( $M_{w,MALLS}$ ) were measured on a triple detector system containing RI detector (Wyatt Technology, Optilab REX), viscometer (Wyatt Technology, ViscoStar), and a multi-angle laser light scattering (MALLS) detector (Wyatt Technology, DAWN EOS) with the light wavelength at 690 nm. Absolute molecular weights were determined using ASTRA software from Wyatt Technology. The pore structures of all samples were assessed from the N<sub>2</sub> isotherm curve measured by a gas adsorption analyzer (NOVA2000 series, Quantachrome Instruments). Nitrogen sorption analysis: Prior to the adsorption experiments, all samples were degassed at 70 °C for at least 24 h to eliminate the surface contaminants (water or oils). The standard analysis of nitrogen sorption isotherms recorded for all samples studied provided the Brunauer-Emmett-Teller (BET) surface area,  $S_{BET}$ , evaluated in the range of relative pressure between 0.04-0.2. The procedures used for the measurement of CO<sub>2</sub> absorption and desorption can be found in a prior publication.<sup>5</sup>

**Preparation of the bromine group modified carbon black by acid oxidation (CB-Br).** A suspension of carbon black (10.0 g) in nitric acid (69.5%, 100 mL) was sonicated for 30 min and the mixture was stirred for 24 h at 100 °C. After cooling to room temperature, the solid was separated by vacuum filtration, and washed with deionized water until the pH reached 7. The product was dried *in vacuo* at 50 °C, giving 9.6 g of the carboxyl group modified carbon black (CB-COOH).

The CB-COOH (3.0 g) was dispersed in SOCl<sub>2</sub> (50 mL) and the mixture was stirred at 65 °C for 24 h. After the excess SOCl<sub>2</sub> was removed under reduced pressure, anhydrous DMF (10 mL) was added to the residue. The mixture was cooled to 0 °C, the mixture of HEBiB (15 g) and anhydrous triethylamine (5 g) was slowly added and then heated to 120 °C for 24 h under nitrogen atmosphere. The solid was

separated by centrifugation and washed repeatedly with deionized water and THF (each time for 30 min, at 12,000 rpm), and then dried *in vacuo* at 50 °C.

**Synthesis of 1-(azidomethyl)-4-(1-bromoethyl)benzene.**<sup>5-7</sup> Sodium azide (13.0 g, 0.2 mol), H<sub>2</sub>O (75 mL), DMF (250 mL), and CMS (15.26 g, 0.1 mol) were added to a 500 mL round bottom flask containing a stir bar. The resulting solution was stirred for 48 h at room temperature under an N<sub>2</sub> atmosphere. The reaction was then diluted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and poured onto H<sub>2</sub>O (400 mL). The layers were separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were then washed with brine, dried over MgSO<sub>4</sub>, and concentrated by rotary evaporation. The crude product was purified by passage through a silica gel column using 1:9 EtOAc:hexane as the eluent and the solution was concentrated by rotary evaporation to give 1-azidomethyl-4-vinyl-benzene. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 4.35 (s, 2H, N<sub>3</sub>CH<sub>2</sub>), 5.30 and 5.79 (d, 2H, CH<sub>2</sub>=CH), 6.74 (m, 1H, CH<sub>2</sub>=CH), 7.3-7.5 (m, 4H, benzene-*H*).

To a stirred suspension of 1-azidomethyl-4-vinyl-benzene (1.59 g, 10 mmol) and SiO<sub>2</sub> (5 g) in CH<sub>2</sub>Cl<sub>2</sub> (25 mL), a solution of PBr<sub>3</sub> (1.08 g, 4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added for 10 min at r.t.. The suspension was subsequently stirred for an additional 30 min and then filtered. The SiO<sub>2</sub> was washed with CH<sub>2</sub>Cl<sub>2</sub> (15 mL), and the combined liquid was washed with NaHCO<sub>3</sub>, brine, and the extracted organic layer was dried over anhydrous MgSO<sub>4</sub>. The solvent was evaporated under reduced pressure to give 1-(azidomethyl)-4-(1-bromoethyl)benzene. The infrared spectrum shows a strong characteristic absorption peak of azide at 2102 cm<sup>-1</sup> (Figure S1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 2.07 (d, 3H, CCH<sub>3</sub>), 4.36 (s, 1H, N<sub>3</sub>CH<sub>2</sub>), 5.23 (m, 1H, CHCH<sub>3</sub>), 7.3-7.5 (m, 4H, benzene-*H*).

**Preparation of the bromine modified carbon black by nitrene chemistry (CB-N-Br).**<sup>5</sup> Pristine carbon black (0.25 g) and NMP (20 mL) were placed in a 50 mL Schlenk flask fitted with a condenser. The mixture was ultrasonicated for 1 h and then placed in an oil bath. 1-(Azidomethyl)-4-(1-bromoethyl)benzene (2.50 g, 10.4 mmol) was added, and the mixture was bubbled with nitrogen for 30 min. The reaction mixture was then heated to around 160 °C under a nitrogen atmosphere for 18 h. After cooling to room temperature, the product was isolated by precipitation into acetone. The resulting

precipitate was redispersed in acetone by ultrasonication and then collected by centrifugation. This process was repeated until the upper layer was nearly colorless. The separated solid was subsequently redispersed in water and purified by five centrifugation cycles, and then redispersed in acetone and purified by three centrifugation cycles. The supernatant was decanted and the black solid was dried *in vacuo* at 60 °C overnight to give CB-N-Br.

**Grafting of hyperbranched polymers from CB-Br (CB-g-PCMS).** The dried CB-Br (100 mg) and DMF (1.8 mL) were added to a Schlenk flask, followed by addition of CMS (3.6 mL, 25.2 mmol), CuCl<sub>2</sub> (0.4 mg), and PMDETA (13.2 μL). The flask was then degassed by five freeze-pump-thaw cycles. During the final cycle, while the contents were frozen in liquid nitrogen, the flask was back filled with nitrogen and CuCl (5.9 mg) was added. The flask was then degassed and back filled with nitrogen thrice. The flask was allowed to warm up to room temperature and an initial sample (t = 0) was collected by syringe. The flask was then placed in an oil bath thermostated at 100 °C. Samples were taken from the flask at timed intervals and the conversion was calculated based on the consumption of double bonds relative to DMF (internal standard) in the reaction mixture measured by <sup>1</sup>H NMR.

**Grafting of hyperbranched polymers from CB-N-Br (CB-N-g-PCMS).**<sup>5</sup> The dried CB-N-Br (100 mg) and DMF (5.19 mL) were added to a Schlenk flask and sonicated for 30 min. CMS (10.37 mL, 73.6 mmol), CuCl<sub>2</sub> (1.2 mg, 0.009 mmol), and PMDETA (38.4 μL, 0.184 mmol) were added to the Schlenk flask. The flask was then degassed by five freeze-pump-thaw cycles. During the final cycle, while the contents were frozen in liquid nitrogen, the flask was back filled with nitrogen and CuCl (17.3 mg, 0.175 mmol) was added. The flask was then degassed and back filled with nitrogen thrice. The flask was allowed to warm up to room temperature and an initial sample (t = 0) was collected by a syringe. The flask was then placed in an oil bath thermostated at 100 °C. Samples were taken from the flask at timed intervals, and the conversion was calculated based on the consumption of double bonds relative to DMF (internal standard) in the reaction mixture measured by <sup>1</sup>H NMR.

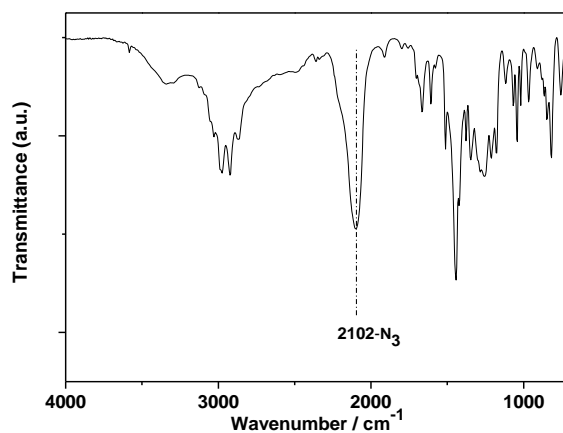
**Preparation of carbon black with DVB crosslinked shells (CB-g-PDVB).** The dried CB-Br (50 mg) and DMF (4.00 mL) were added to a Schlenk flask and sonicated for 30 min. DVB (0.22 mL, 1.58

mmol), CuCl<sub>2</sub> (0.8 mg), and PMDETA (27.6 μL) were then added. The flask was then degassed by five freeze-pump-thaw cycles. During the final cycle, while the contents were frozen in liquid nitrogen, the flask was back filled with nitrogen and CuCl (12.5 mg) was added. The flask was then degassed and back filled with nitrogen thrice. The flask was allowed to warm up to room temperature and an initial sample (t = 0) was collected by syringe. The flask was then placed in an oil bath thermostated at 100 °C. At timed intervals, samples were taken and the conversion was calculated based on the consumption of double bonds relative to DMF (internal standard) in the reaction mixture measured by <sup>1</sup>H NMR.

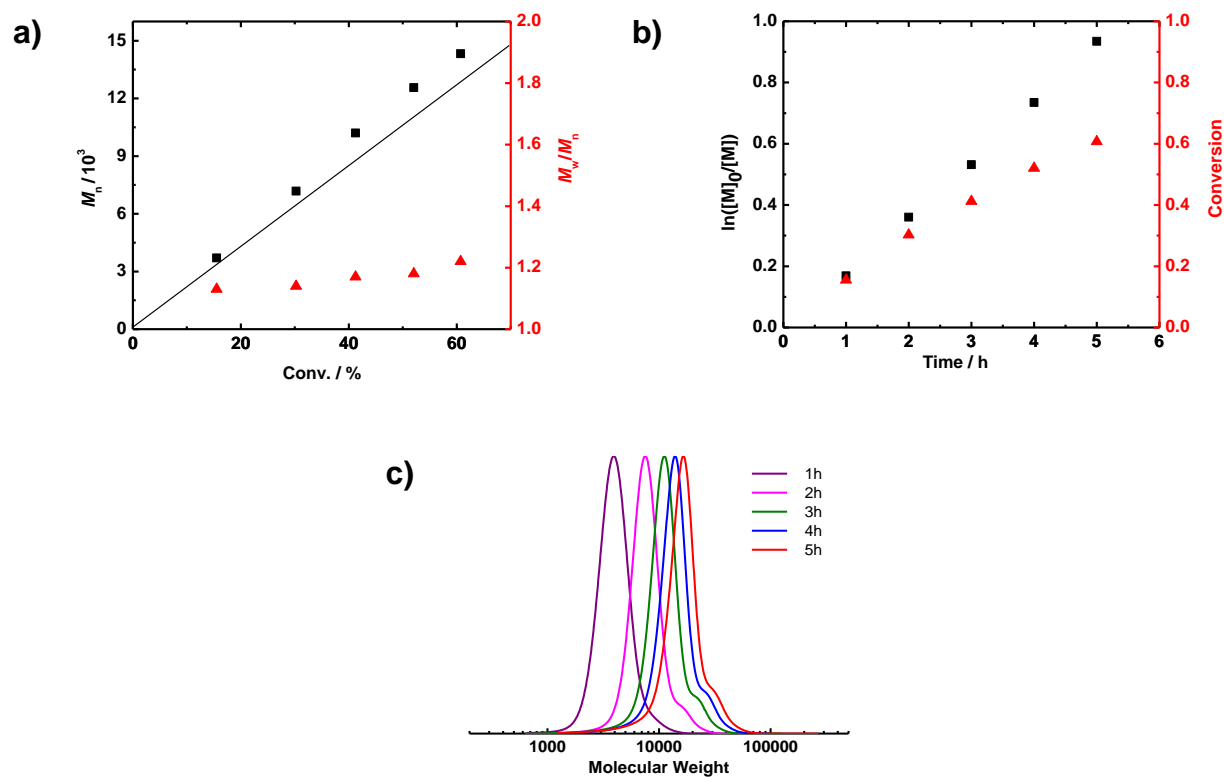
**One-pot two-step grafting of crosslinked hyperbranched polymers from carbon black (CB-g-xPCMS).** The dried CB-Br (100 mg) and DMF (8.00 mL) were added into a Schlenk flask and sonicated for 30 min. DVB (0.44 mL, 3.15 mmol), CuCl<sub>2</sub> (0.8 mg), and PMDETA (55.2 μL) were then added. The flask was then degassed by five freeze-pump-thaw cycles. During the final cycle, while the contents were frozen in liquid nitrogen, the flask was back filled with nitrogen and CuCl (25.0 mg) was added. The flask was then degassed and back filled with nitrogen thrice. The flask was allowed to warm up to room temperature and an initial sample (t = 0) was collected by syringe. The flask was then placed in an oil bath thermostated at 100 °C. At timed intervals, samples were drawn and the conversion was calculated based on the consumption of double bonds relative to DMF (internal standard) in the reaction mixture observed by <sup>1</sup>H NMR. After 25 h, the conversion of DVB reached 14.3%, and then 3.55 mL of N<sub>2</sub>-bubbled CMS (25.2 mmol) was added to the reaction solution. Samples were taken at timed intervals and analyzed by <sup>1</sup>H NMR to determine the conversions of DVB and CMS. The polymerization was stopped at 110 h by opening the flask and exposing the catalyst to air. The sample was washed repeatedly with THF and separated by centrifugation (12, 000 rpm, 1 h), and then dried *in vacuo* at 50 °C overnight.

**Introduction of hydroxide groups onto the surface of polymer-grafted carbon black.** Typically, polymer-grafted carbon black (100 mg) was mixed with trimethylamine (35% ethanol solution, 10 mL). The mixture was sonicated, and then stirred at r.t. for 1 d. The reaction mixture was separated by centrifugation and washed repeatedly with methanol. Then the sample was mixed with KOH (0.2 g/mL

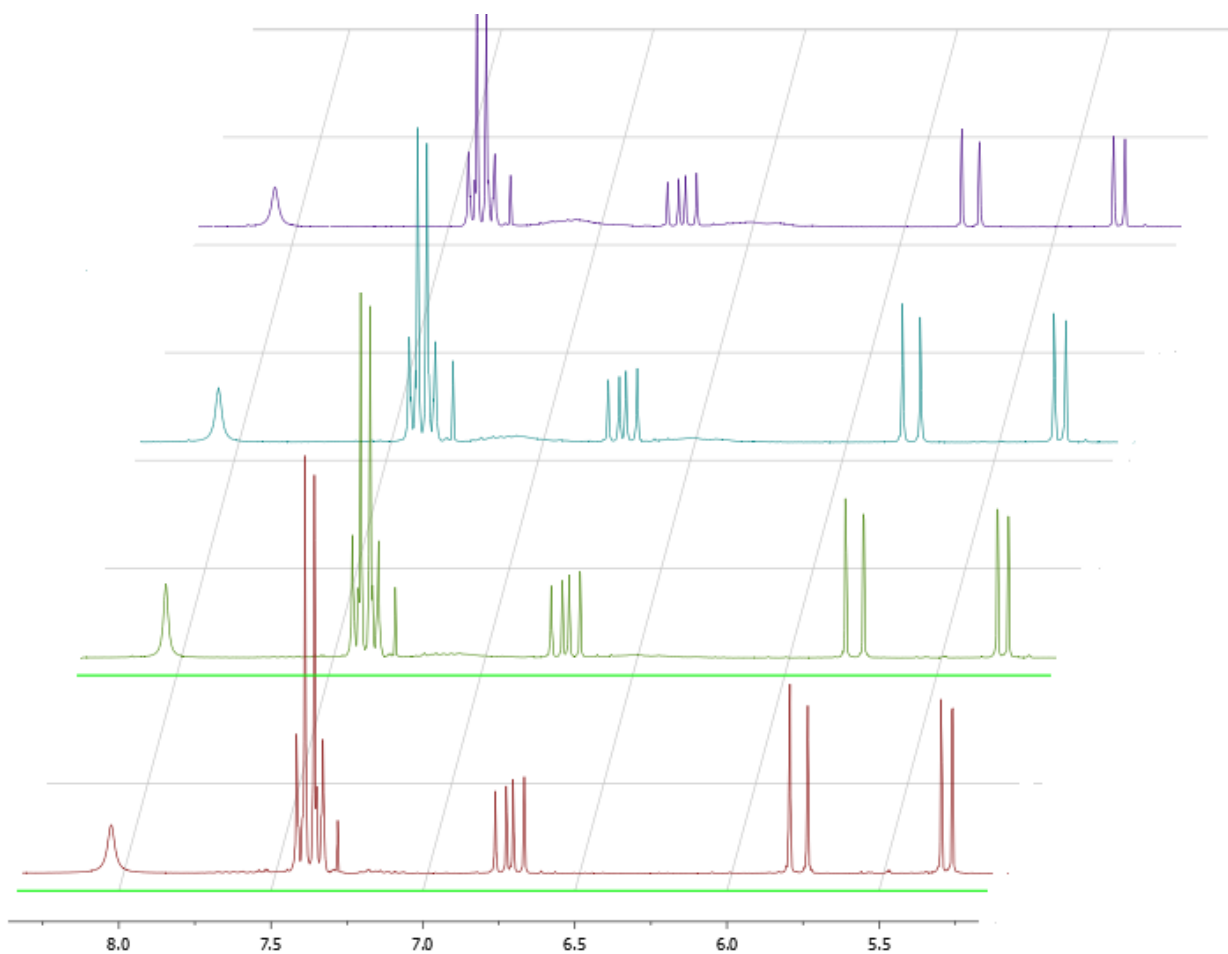
aqueous solution, 15 mL). The mixture was sonicated and stirred at r.t. for 1 d. The reaction mixture was separated by centrifugation and washed repeatedly with methanol and dried *in vacuo* at 50 °C.



**Figure S1.** IR result of 1-(azidomethyl)-4-(1-bromoethyl)benzene.

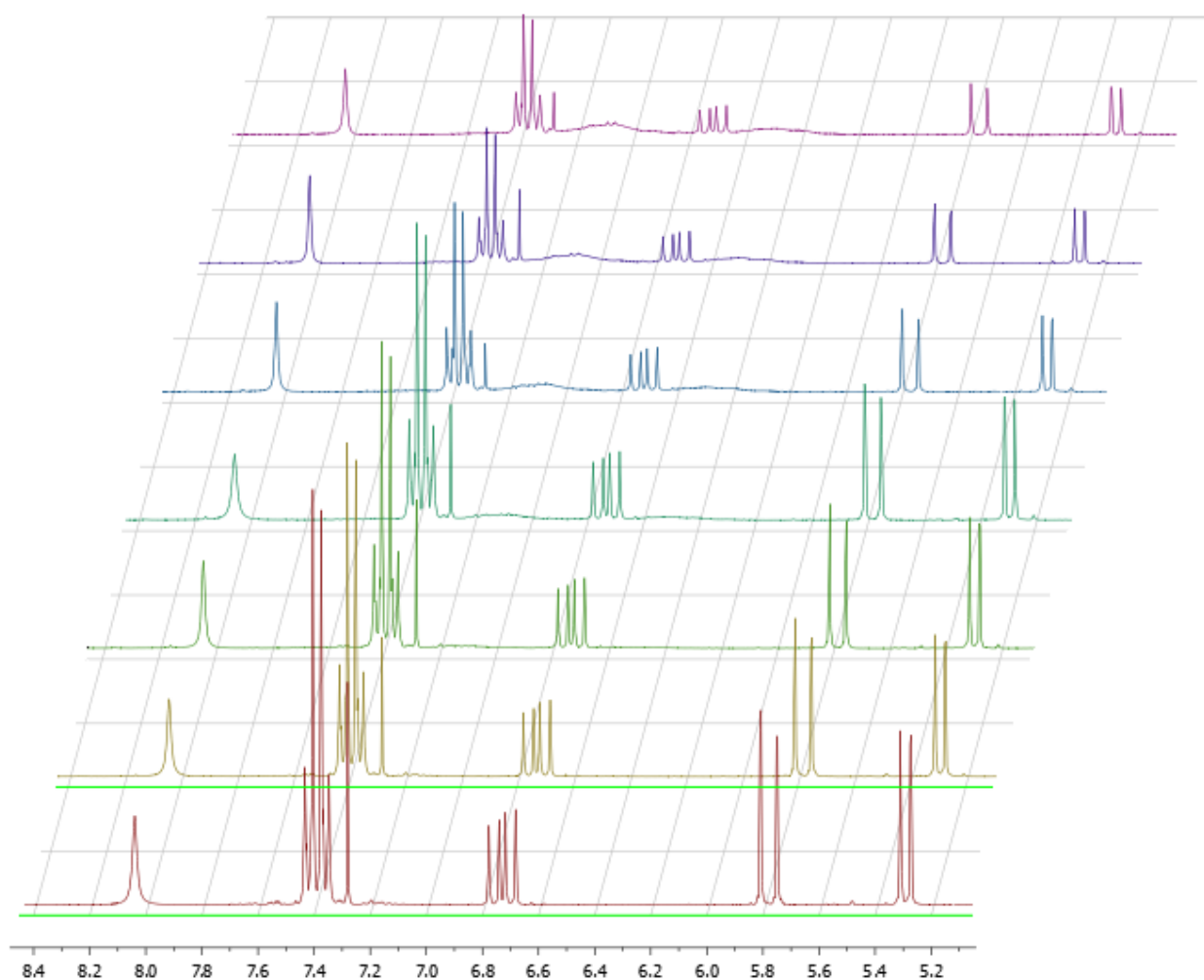


**Figure S2.** Plot of  $M_n$  and  $M_w/M_n$  vs. conversion (a), plot of  $\ln([M]_0/[M])$  and conversion vs. time (b), and GPC traces (c).  $[St]_0/[AMBE]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 400/1/0.95/0.05/1$ ,  $St/anisole = 5/1(v/v)$ , at 90 °C.

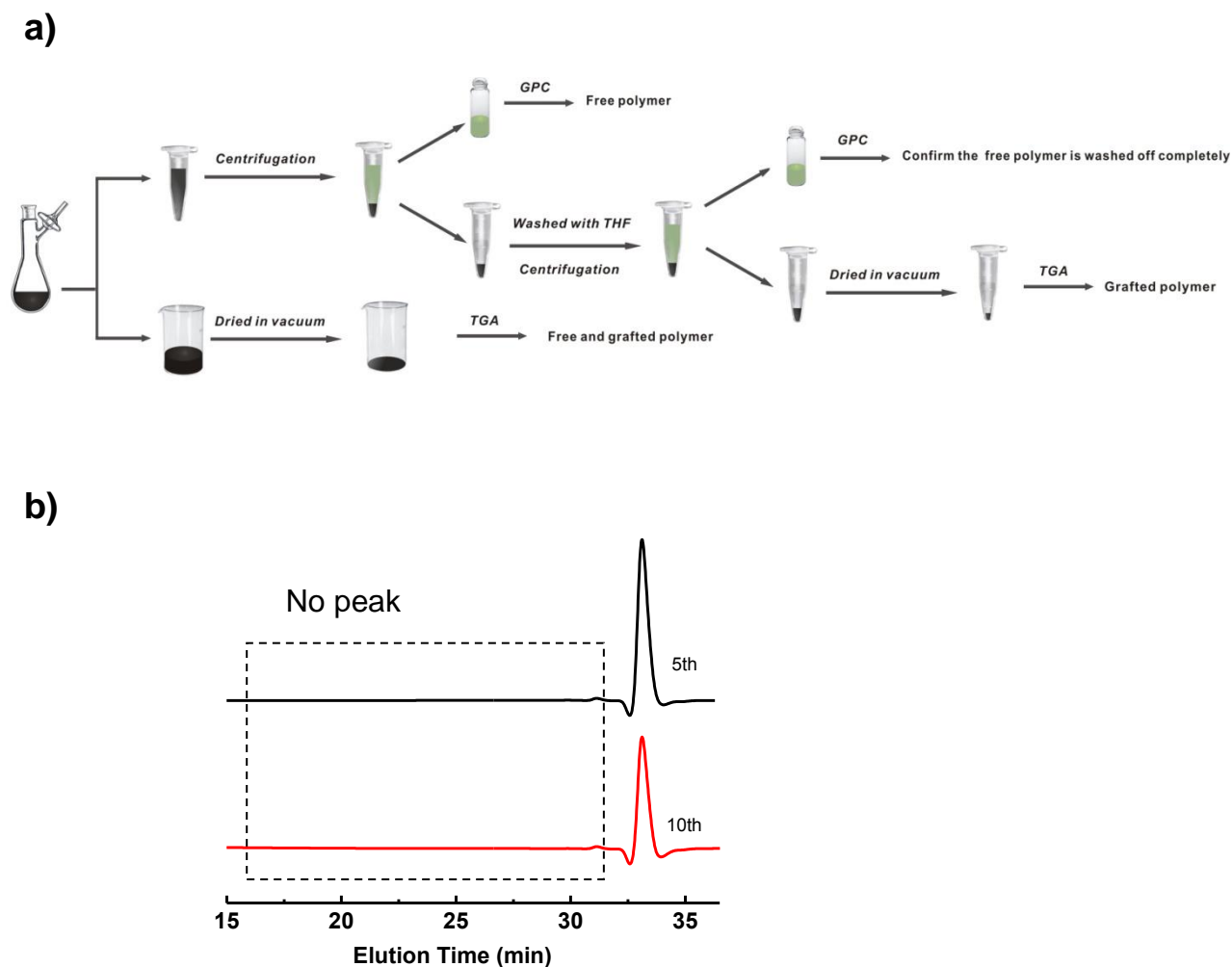


**Figure S3.** <sup>1</sup>H-NMR spectra of the free polymers in the reaction system: 4 h, 13 h, 24 h, and 42 h (from bottom to top). [CB-Br]<sub>0</sub>/[CMS]<sub>0</sub>/[CuCl]<sub>0</sub>/[CuCl<sub>2</sub>]<sub>0</sub>/[PMDETA]<sub>0</sub> = 1/400/0.95/0.05/1, DMF/CMS = 1/2 (v/v), 100°C. The peaks from the vinyl group in *p*-chloromethylstyrene (at 6.7, 5.8, and 5.3 ppm) gradually decreased compared to that of the internal standard DMF (at 8.1 ppm).



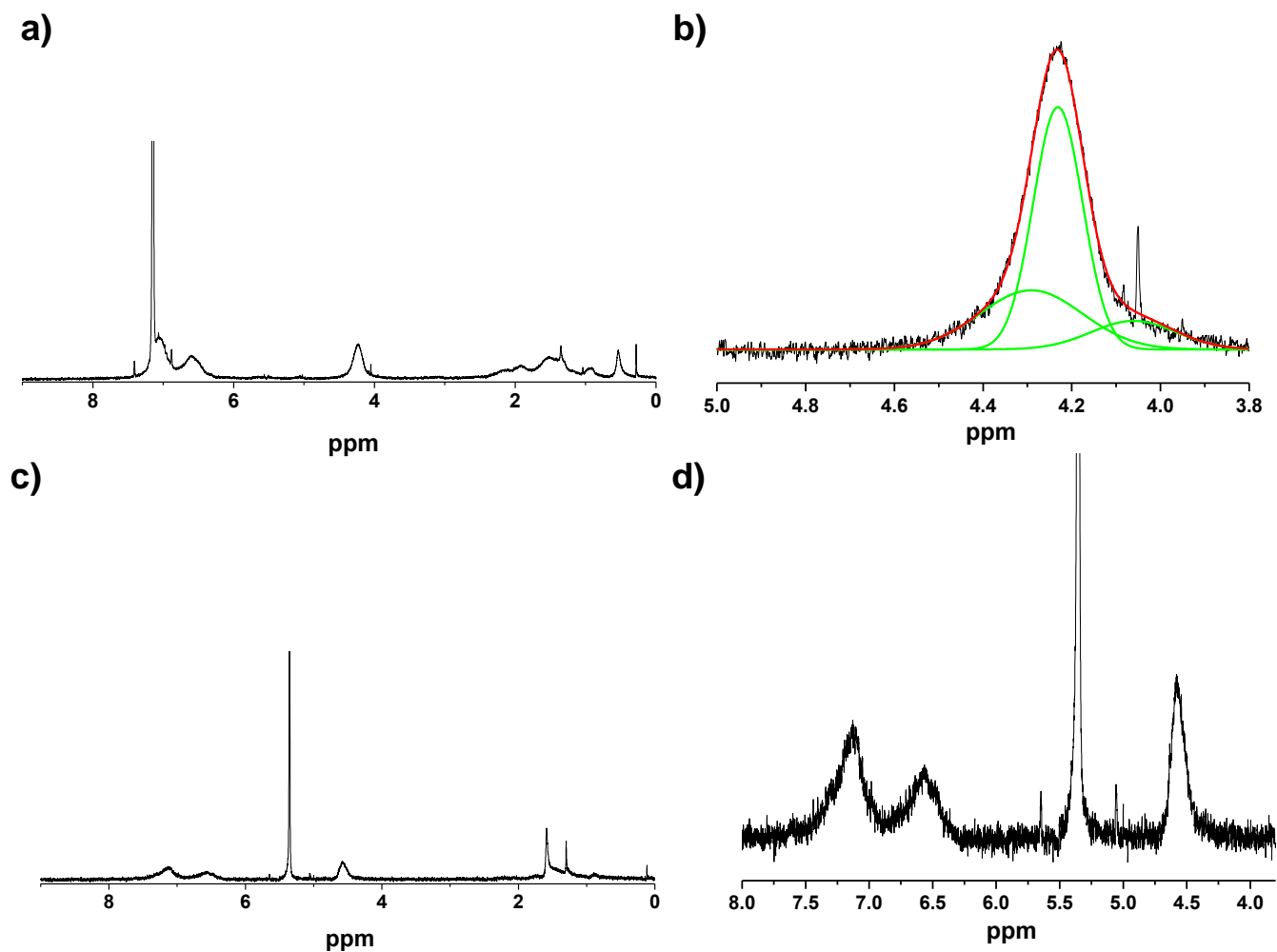
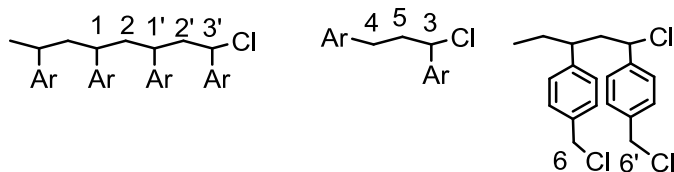


**Figure S4.** <sup>1</sup>H NMR spectra of the free polymers in the reaction system: 4 h, 12 h, 24 h, 42 h, 72 h, and 96 h (from bottom to top). [CB-N-Br]<sub>0</sub>/[CMS]<sub>0</sub>/[CuCl]<sub>0</sub>/[CuCl<sub>2</sub>]<sub>0</sub>/[PMDETA]<sub>0</sub> = 1/400/0.95/0.05/1, DMF/CMS = 1/2(v/v), 100°C. The peaks from the vinyl group in *p*-chloromethylstyrene (at 6.7, 5.8, and 5.3 ppm) gradually decreased compared to that of the internal standard DMF (at 8.1 ppm).



**Figure S5.** (a) Method for the measurement of the free polymer and grafted polymer in the reaction system. (b) GPC traces of the upper THF solutions in the fifth and tenth centrifugation cycles.

The deposited carbon black sample at the bottom of the centrifugation tube was repeatedly washed with THF. The upper THF solutions in the fifth and tenth centrifugation cycles were measured by GPC. It shows that there was no free polymer detected in the upper solution by GPC.



**Figure S6.** <sup>1</sup>H NMR spectra of free polymer in the reaction solution of CB-N-g-PCMS-96 h: 1) with C<sub>6</sub>D<sub>6</sub> as the solvent: full spectrum (a), and region of CHCl and CH<sub>2</sub>Cl protons (b); 2) with CD<sub>2</sub>Cl<sub>2</sub> as the solvent: full spectrum (c), and region of CHCl and CH<sub>2</sub>Cl protons (d).<sup>8</sup>

The peak of 6' is at 4.06 ppm and has an integrated area of 0.80.

The peak of 6 is at 4.23 ppm and has an integrated area of 3.94.

The peak of 3+3' is at 4.29 ppm and has an integrated area of 2.00.

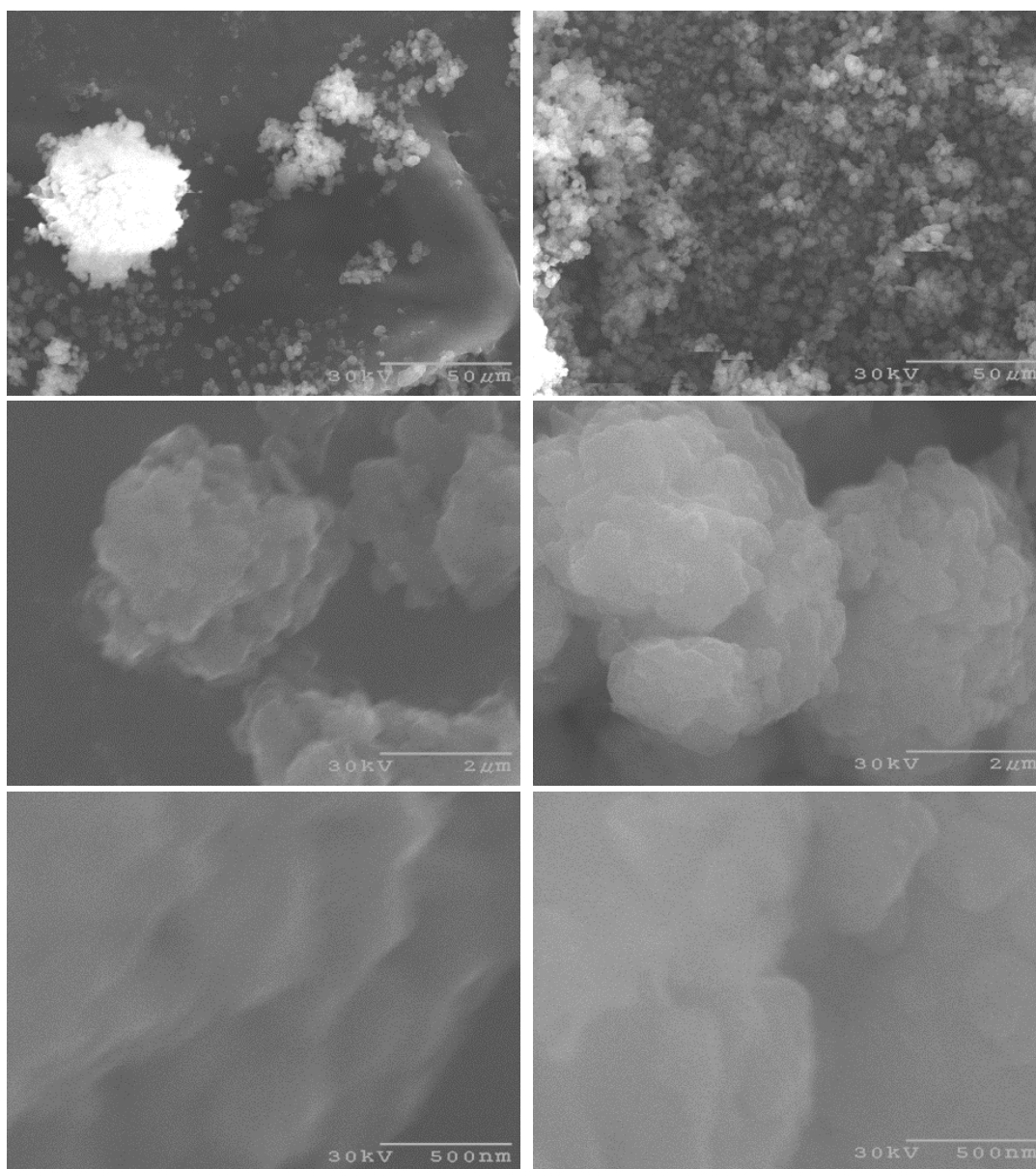
$$I(T) = I_{6'}/2 = 0.80/2 = 0.40$$

$$I(L_V) = I_6/2 = 3.94/2 = 1.97$$

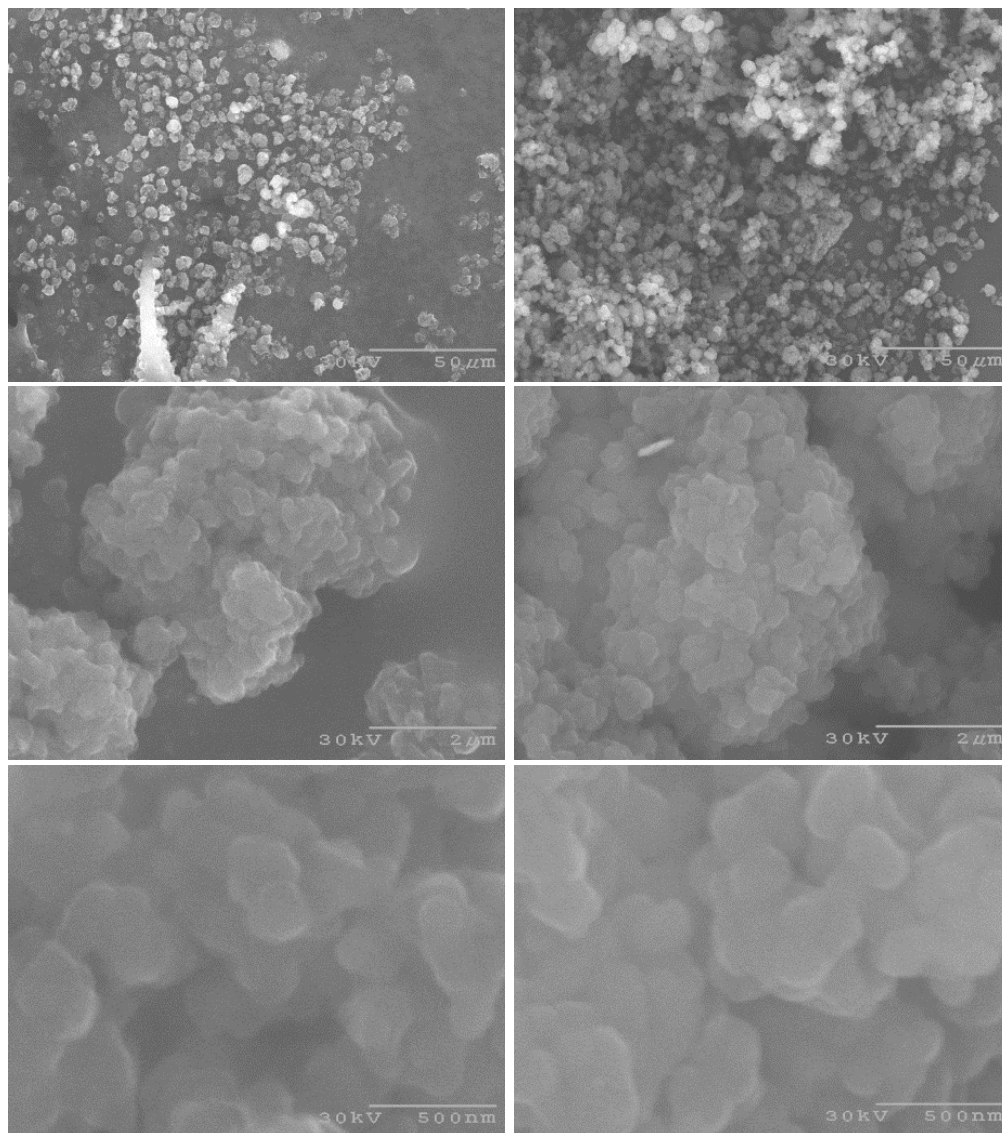
$$I(L_C) = I_{(3+3')} - I(T) = 2.00 - 0.40 = 1.60$$

$$I(D) = I_{Ar}/4 - I(T) - I(L_V) - I(L_C) = 21.31/4 - 0.40 - 1.97 - 1.60 = 1.36$$

$$DB = 2I(D) / (2I(D) + I(L_V) + I(L_C)) = 0.43$$



**Figure S7.** SEM images of CB-N-g-PCMS-OH<sup>-</sup> without (left column) and with (right column) Au coated



**Figure S8.** SEM images of CB-N-Br-OH without (left column) and with (right column) Au coated

## References

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