Supporting Information (SI) for Journal of Materials Chemistry A

Carbohydrate based hyper-cross-linked organic polymers with –OH functional group for CO_2 separation†

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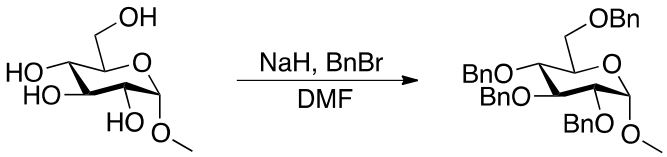
1. Experimental details

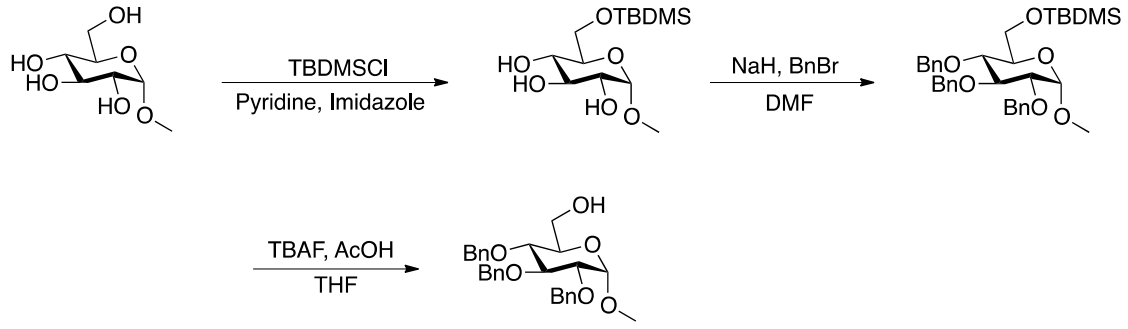
1.1 General carbohydrate monomer synthesis

All chemicals were purchased as reagent grade and used without further purification, unless otherwise noted. Reagent grade dichloromethane (DCM), tetrahydrofuran (THF), methanol (MeOH) and N, N-dimethylformamide (DMF) were obtained from the Pure-Solv (Innovation Technologies) solvent system that uses alumina columns, except for DMF, which was dried over a column of 5Å molecular sieves. Pyridine was distilled over CaH_2 prior to use. All reactions were performed under anhydrous conditions unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) on silica gel precoated aluminum plates. Zones were detected by UV irradiation using a 254 nm lamp and/or by heat/charring with *p*-anisaldehyde–sulfuric acid development reagent. Column chromatography was performed on silica gel (40−63 μm). ^{1}H and ^{13}C NMR spectra were recorded at room temperature with a Varian VNMRS 500 MHz or a Varian VNMRS 600 instrument. Chemical shifts are reported in δ-units (ppm) relative to the residual ^{1}H $CDCl_3$ at δ 7.26 ppm and ^{13}C at δ 77.16 ppm. Mass spectrometric analysis was performed on a QSTAR Elite quadrupole time-of-flight (QTOF) mass spectrometer with an ESI source. Compounds **Glc-3** and **Ara-1** were purchased from Sigma−Aldrich and compound **Gal-1** was purchased from Santa Cruz Biotechnology. Compounds **Glc-1**,[S1] **Glc-2**,[S2] and **Gal-2**[S2] are synthesized on the base of literature procedures.



Glc-1

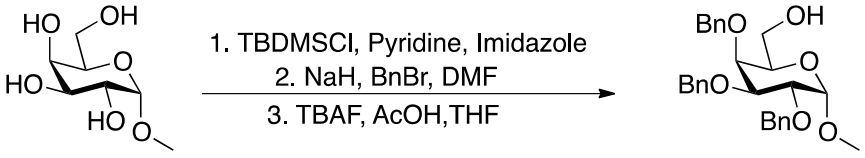
Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (**Glc-1**): Methyl α-D-glucopyranoside (500 mg, 2.57 mmol) was dissolved in dry DMF (10 mL). The solution was cooled to 0 °C and added NaH (60%, 824 mg, 20.60 mmol) portionwise. After stirring for 15 min, benzyl bromide (1.84 mL, 15.45 mmol) was slowly added and the reaction mixture was warmed to room temperature. After stirring overnight, the reaction mixture was quenched by adding methanol (5 mL) and concentrated *in vacuo*. The resulting residue was mixed with water (100 mL) and extracted with methylene chloride (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by silica gel chromatography (Hexanes:EtOAc=15:1 to 7:1) to yield **Glc-1** (1.24 g, 87%) as colorless oil. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.42 – 7.20 (m, 20H), 5.06 (d, *J* = 10.9 Hz, 1H), 4.90 (d, *J* = 5.1 Hz, 1H), 4.89 (d, *J* = 5.2 Hz, 1H), 4.86 (d, *J* = 12.1 Hz, 1H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.70 (d, *J* = 3.5 Hz, 1H, H-1), 4.67 (d, *J* = 12.2 Hz, 1H), 4.55 (d, *J* = 3.1 Hz, 1H), 4.53 (d, *J* = 4.4 Hz, 1H), 4.06 (t, *J* = 9.3 Hz, 1H), 3.82 (m, 1H), 3.78 (dd, *J* = 10.5, 3.8 Hz, 1H), 3.72 – 3.68 (ddd, *J* = 10.0, 5.3, 3.2 Hz, 2H), 3.63 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ 138.92, 138.38, 138.29, 138.04, 128.58 – 127.71 (Ar-C), 98.37, 82.29, 79.99, 77.82, 75.89, 75.21, 75.13, 73.61, 70.21, 68.60, 55.32. HRMS ESI (m/z) $(M+Na)^+$ calcd for $C_{35}H_{38}O_6Na^+$ 577.2566, found 577.2566. The data of **Glc-1** are consistent with those previously reported.[S1]



Glc-2

Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (Glc-2). A solution of Methyl α-D-glucopyranoside (400 mg, 2.06 mmol) in anhydrous pyridine (10 mL) was added imidazole (280 mg, 4.12 mmol) and cooled to 0 °C. Then *tert*-butylchlorodimethylsilane (372 mg, 2.47 mmol) was added, and the mixture was stirred at room temperature for 24 h. The reaction mixture was

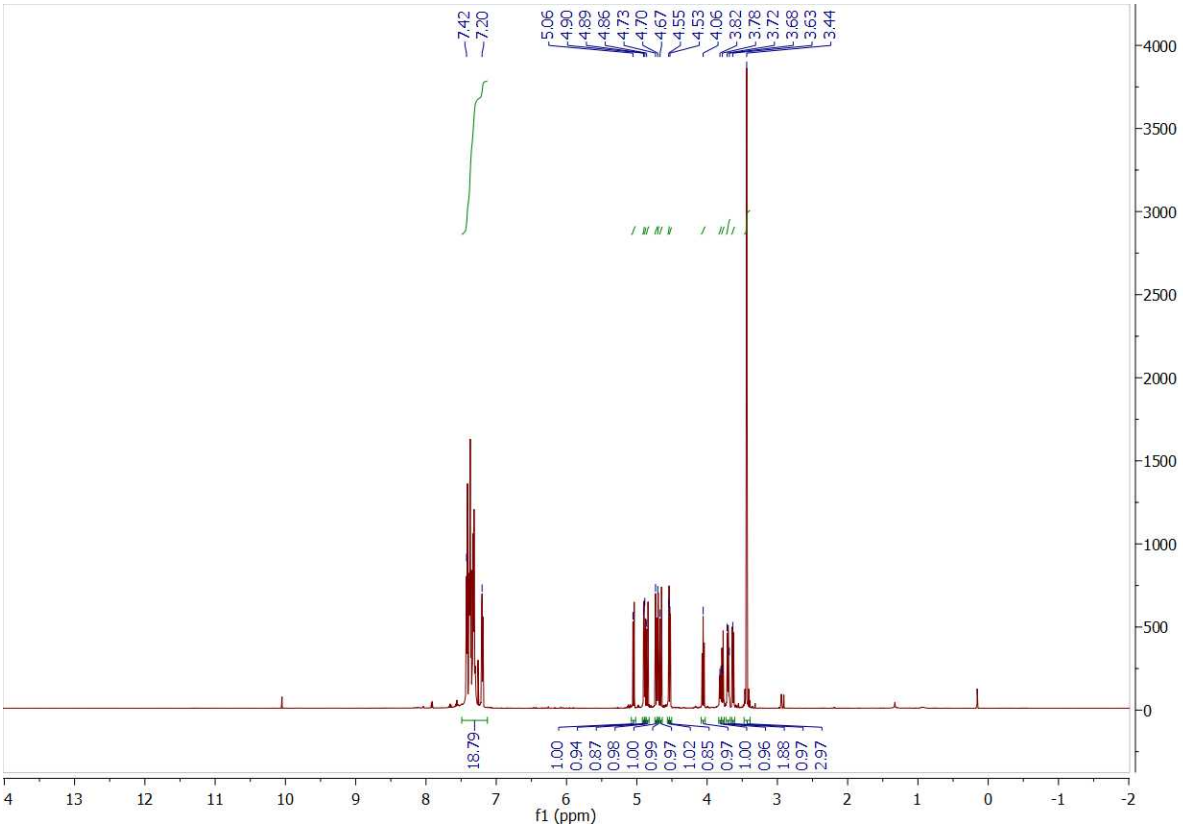
quenched by adding water and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (Hexanes:EtOAc:CH_2Cl_2:MeOH=6:1:1:0.5) to afford methyl 6-*O*-(*tert*-butyldimethylsilyl)-α-D-glucopyranoside (527 mg, 83%) as a white solid. It was then dissolved in anhydrous DMF (10 mL) and cooled to 0 °C. The solution was treated with NaH (60%, 547 mg, 13.68 mmol) portionwise and stirred at 0 °C for 15 min. Benzyl bromide (1.2 mL, 10.26 mmol) was slowly added and the reaction mixture was warmed to room temperature. After stirring overnight, the reaction mixture was quenched by adding methanol (5 mL) and concentrated *in vacuo*. The resulting residue was mixed with water (100 mL) and extracted with methylene chloride (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by silica gel chromatography (Hexanes:EtOAc=20:1 to 8:1) to yield methyl 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-glucopyranoside (690 mg, 70%) as a white solid. It was then dissolved in anhydrous THF (10 mL) and added tetrabutylammonium fluoride solution (1.0 M in THF, 2.39 mmol). The resulting mixture was stirred at room temperature for 16 h. After concentration, the mixture was quenched by water (100 mL) and extracted with methylene chloride (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated again. The crude product was purified by silica gel chromatography (Hexanes:EtOAc=3.5:1) to yield **Glc-2** (431 mg, 78%) as colorless oil. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.41–7.31 (15 H, m), 5.04 (d, *J* = 10.9 Hz, 1H), 4.93 (d, *J* = 11.0 Hz, 1H), 4.89 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 12.1 Hz, 1H), 4.71–4.69 (dd, *J* = 11.6, 8.5 Hz, 2H), 4.62 (d, *J* = 3.5 Hz, 1H, H-1), 4.06 (m, 1H), 3.81 (dd, *J* = 11.8, 2.6 Hz, 1H), 3.74 (dd, *J* = 11.8, 4.1 Hz, 1H), 3.69 (ddd, *J* = 10.0, 4.1, 2.7 Hz, 1H), 3.59 (m, 1H), 3.53 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.40 (s, 3H), 1.96 (s, 1H). ^{13}C NMR ($CDCl_3$, 151 MHz) δ 138.77, 138.18, 138.14, 128.50, 128.43, 128.14, 128.04, 127.99, 127.97, 127.88, 127.64, 98.19, 81.98, 80.01, 77.43, 75.77, 75.05, 73.43, 70.75, 61.80, 55.21. HRMS ESI (m/z) $(M+Na)^+$ calcd for $C_{28}H_{32}O_6Na^+$ 487.2097, found 487.2094. The data of **Glc-2** are consistent with those previously reported.[S2]



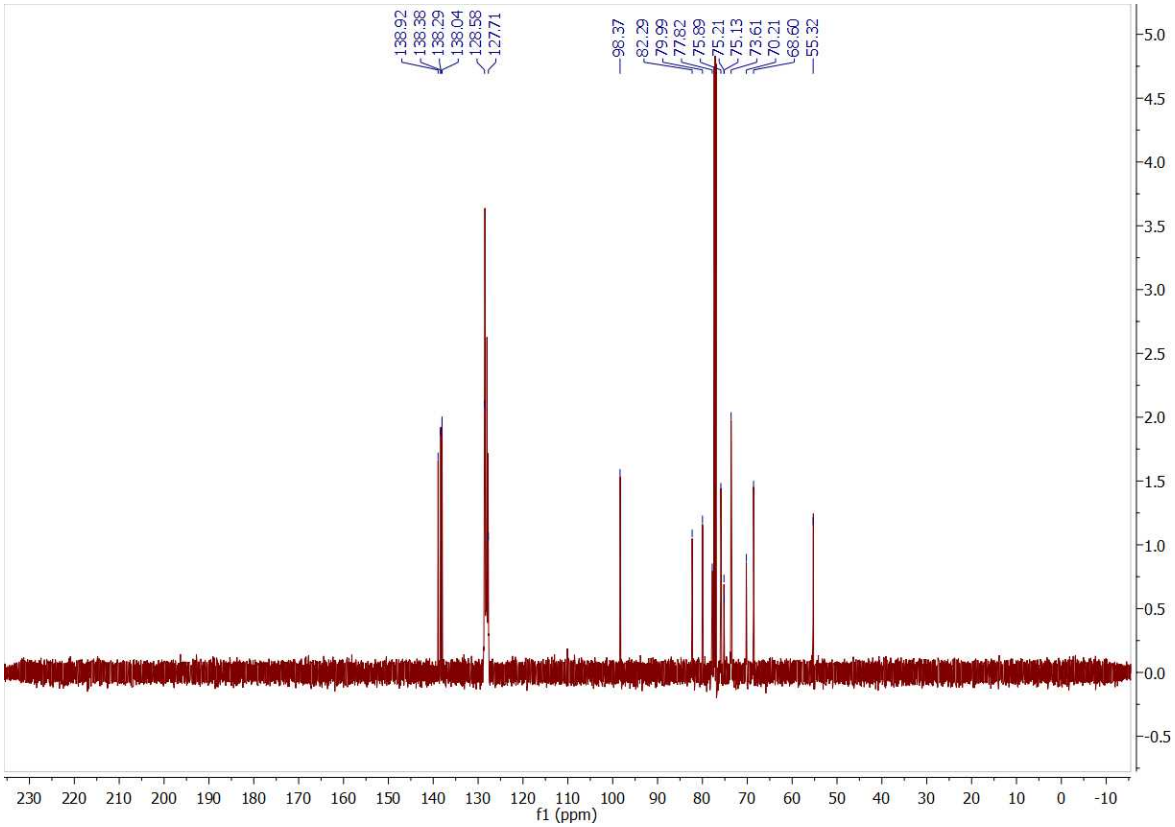
Gal-2

Methyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranoside (Gal-2). A similar synthetic procedure for preparing **Glc-2** was used. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.29 (m, 15H) 5.00 (d, *J* = 11.6 Hz, 1H), 5.00 – 4.90 (m, 2H), 4.78 (d, *J* = 11.7 Hz, 1H), 4.72 (m, 2H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.08 (dd, *J* = 10.1, 3.6 Hz, 1H), 3.96 (dd, *J* = 10.1, 2.8 Hz, 1H), 3.89 (dd, *J* = 2.9, 1.0 Hz,

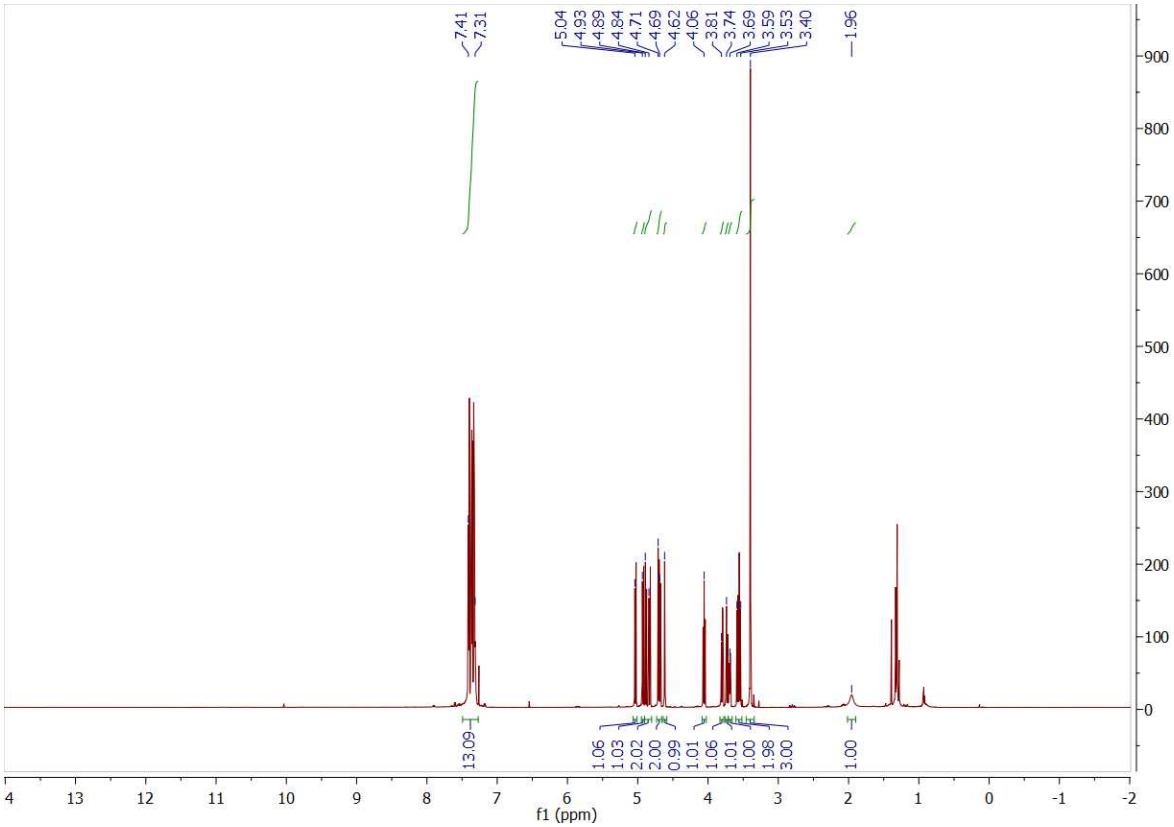
1H), 3.73 (m, 2H), 3.50 (m, 1H), 3.38 (s, 3H), 1.79 (s, 1H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 138.82, 138.53, 138.28, 128.67, 128.57, 128.54, 128.47, 128.19, 128.08, 127.85, 127.72, 127.66, 98.93, 79.22, 76.58, 75.20, 74.55, 73.72, 73.69, 70.37, 62.49, 55.46. HRMS ESI (m/z) $(M+Na)^+$ calcd for $C_{28}H_{32}O_6Na^+$ 487.2097, found 487.2095. The data of **Gal-2** are consistent with those previously reported.[S2]



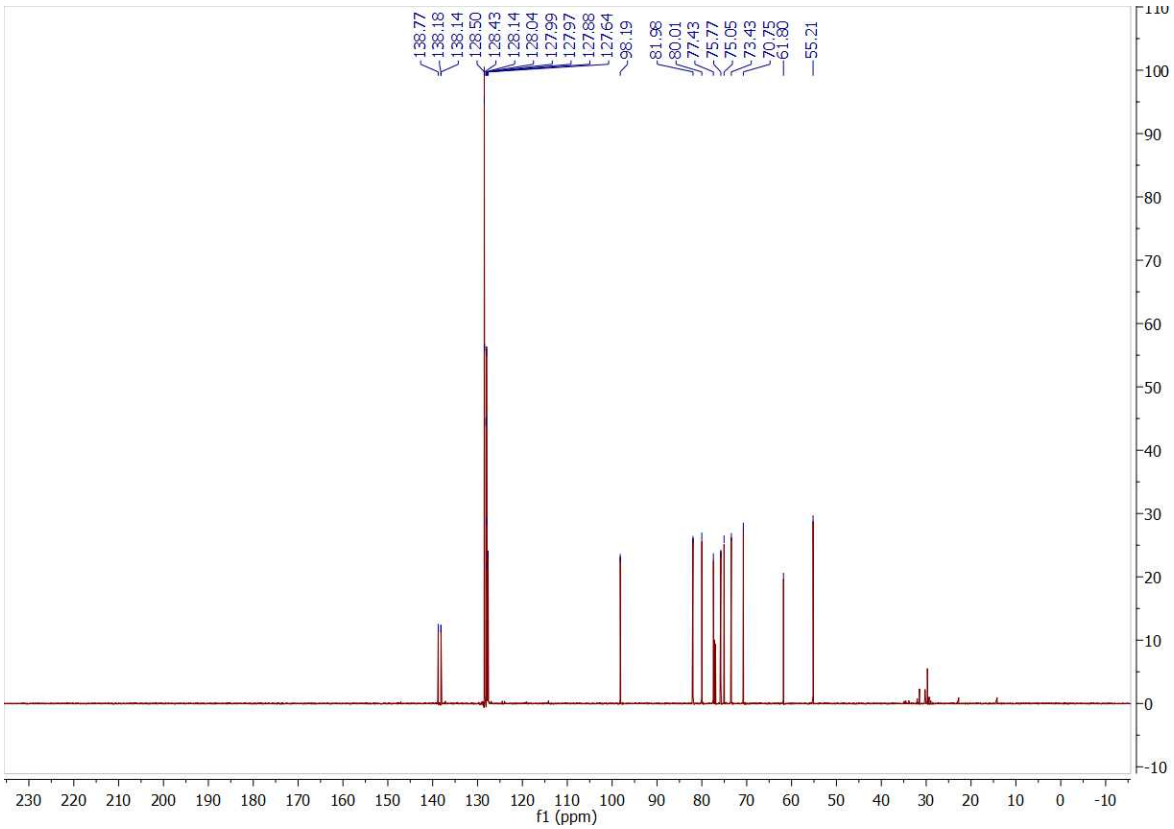
^{1}H NMR Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (**Glc-1**)



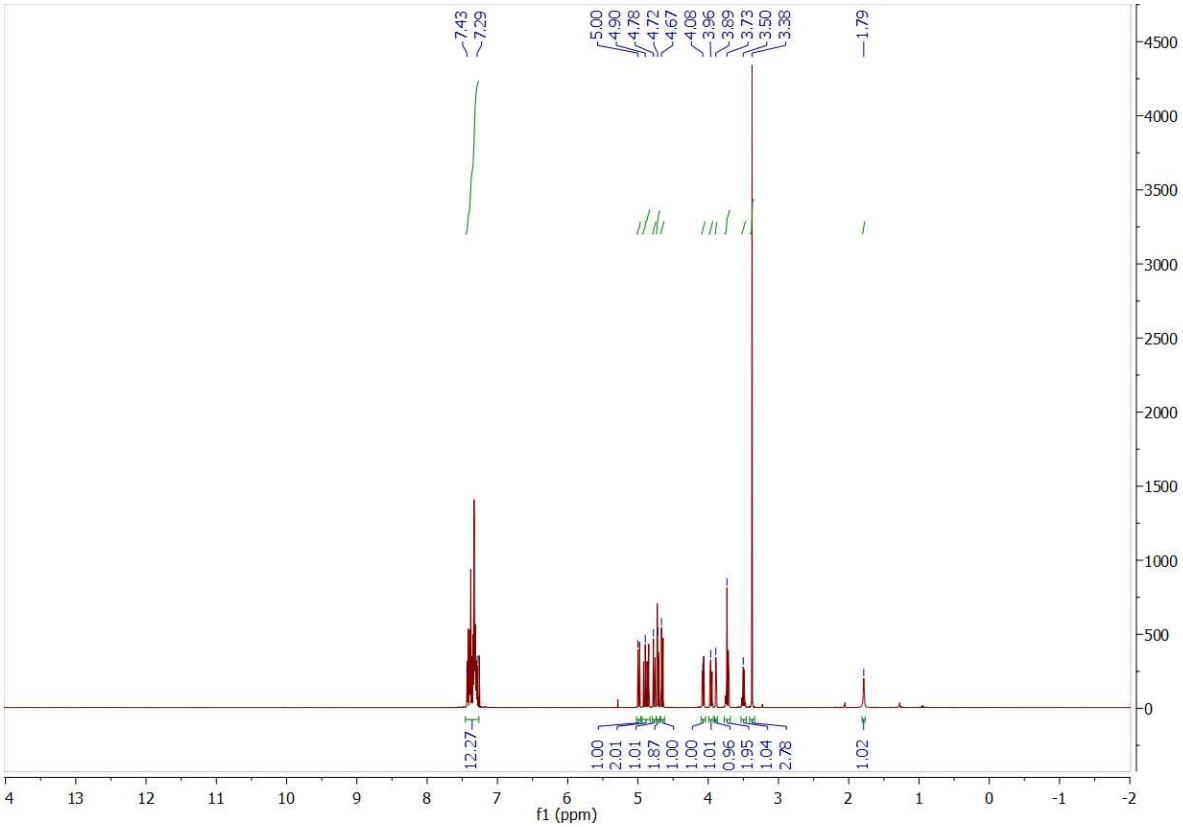
^{13}C NMR Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (**Glc-1**)



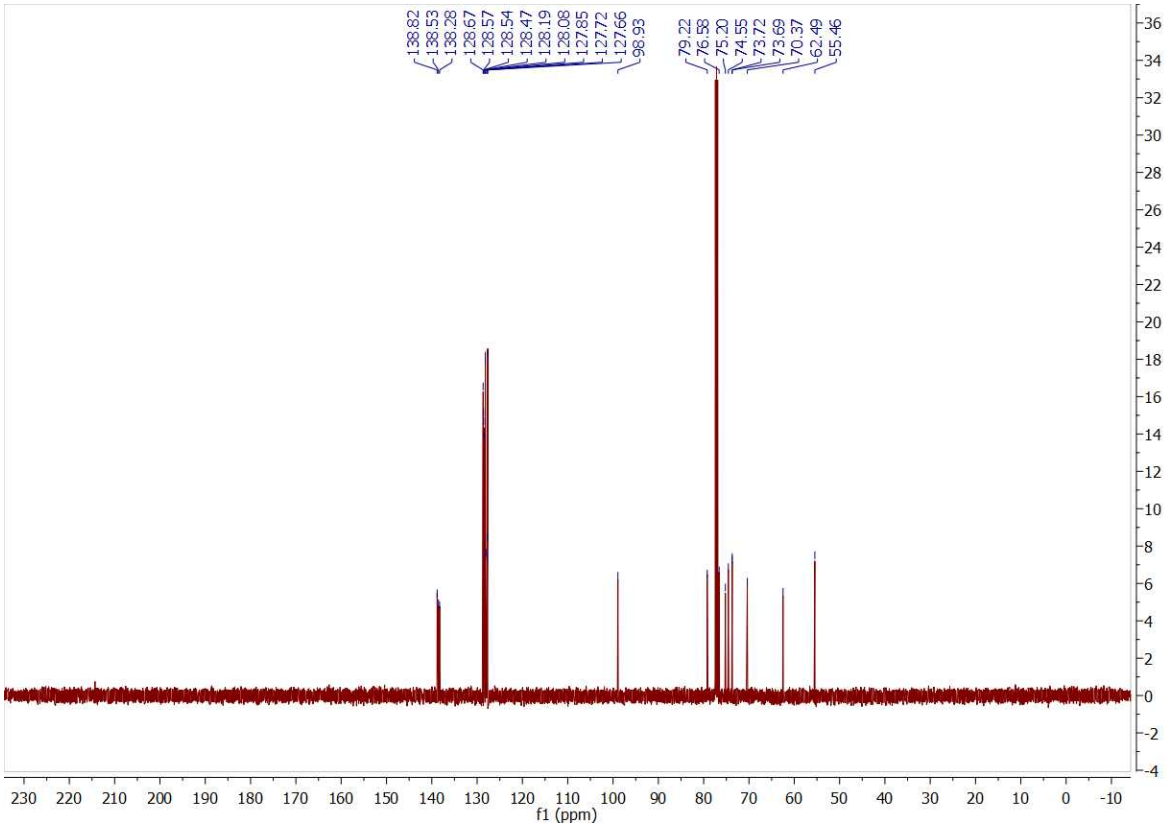
^{1}H NMR Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**Glc-2**)



^{13}C NMR Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**Glc-2**)



^{1}H NMR Methyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranoside (**Gal-2**)



^{13}C NMR Methyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranoside (**Gal-2**)

1.2 General polymerization of benzylated carbohydrates

Typically, to a solution of the monomer and FDA in anhydrous 1,2-dichlorehane (10mL), a slurry of $FeCl_3$ in DCE (10mL) was slowly added under nitrogen atmosphere. The mixture was then heated to 45°C for 5h and 80°C for 19h. The resulting brown precipitate was collected and washed with methanol and water until the filtrate became colorless and further purified by Soxhlet Extraction with methanol for 24h. The polymer was dried under vacuum for 24h at 60°C. For different monomers, the ratio of external cross-linker FDA and catalysis $FeCl_3$ was adjusted because of the diverse numbers of benzyl rings as illustrated in Table S1.

Table S1 composition and porosity of samples

	FDA[a]	$FeCl_3$[a]	S_{micro}(m^2/g)[b]	V_{total} (cm^3 g^{-1})[c]	V_{micro} (cm^3 g^{-1})[d]	S_{micro}/S_{BET}	V_{micro}/V_{total}
Glc-1	8	8	445	0.40	0.20	60.5%	50%
Glc-2	6	6	456	0.47	0.21	55.9%	44%
Glc-3	8	8	479	0.47	0.22	57.7%	46%
Gal-1	8	8	482	0.47	0.22	56.1%	46%
Gal-2	6	6	314	0.93	0.14	28.8%	15%
Ara-1	2	2	237	0.30	0.11	50.4%	35%

[a] Molar ratio with respect to monomer. [b] Micropore surface area calculated form the nitrogen isotherm at P/Po= using T method. [c] Pore volume calculated from nitrogen isotherm at P/Po=0.889. [d] Micropore volume calculated form the nitrogen isotherm using T-method.

Table S2 the BET surface area of all the samples after water treatment (PH=5, 80°C, 48h)

	S_{BET}(m^2/g)	S_{BET} after treatment (m^2/g)	S_{BET} percentage (%)	V_{micro} (cm^3 g^{-1})	V_{micro} after treatment (cm^3 g^{-1})	V_{micro} percentage (%)
Glc-1	735	672	91.4	0.20	0.18	92
Glc-2	816	702	86.1	0.21	0.18	87
Glc-3	829	753	90.9	0.22	0.21	94
Gal-1	858	801	93.4	0.22	0.21	97
Gal-2	1090	1054	96.7	0.14	0.14	99
Ara-1	470	410	87.3	0.11	0.09	84

1.3 Characterization of polymers

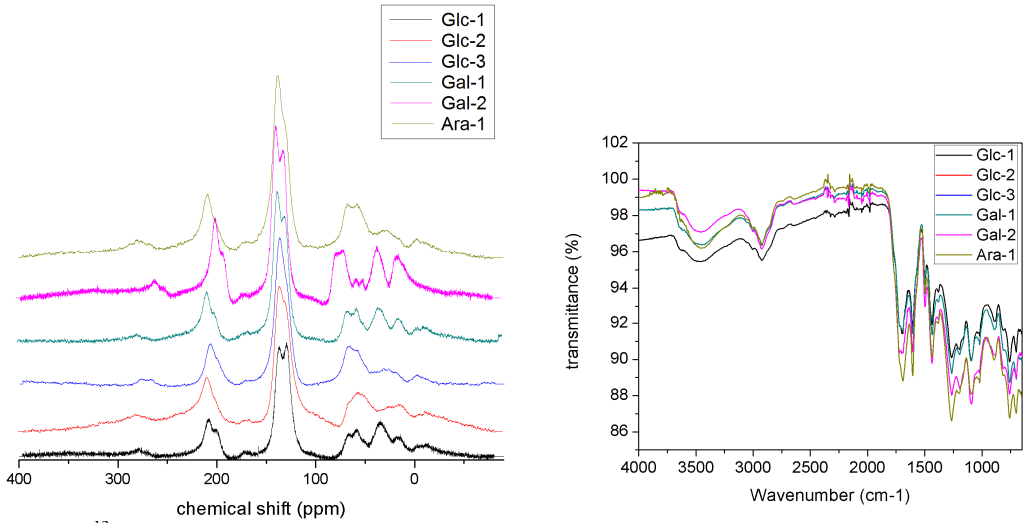


Figure S1. ^{13}C solid state NMR with spinning rate of 7k and FTIR spectrums for all carbohydrate HCPs.

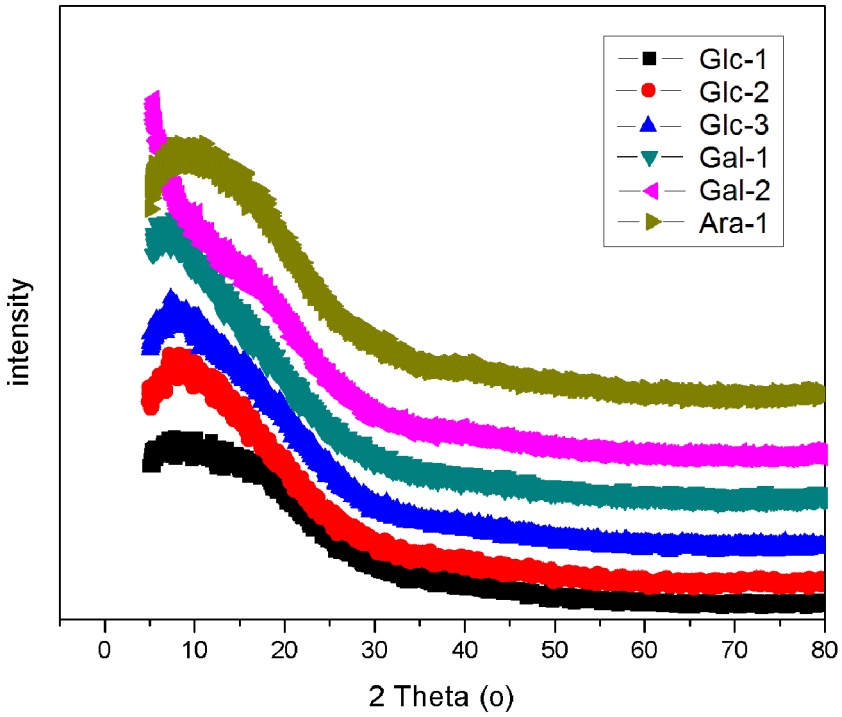


Figure S2. X-ray powder diffraction (XRD) spectra of all carbohydrate polymers.

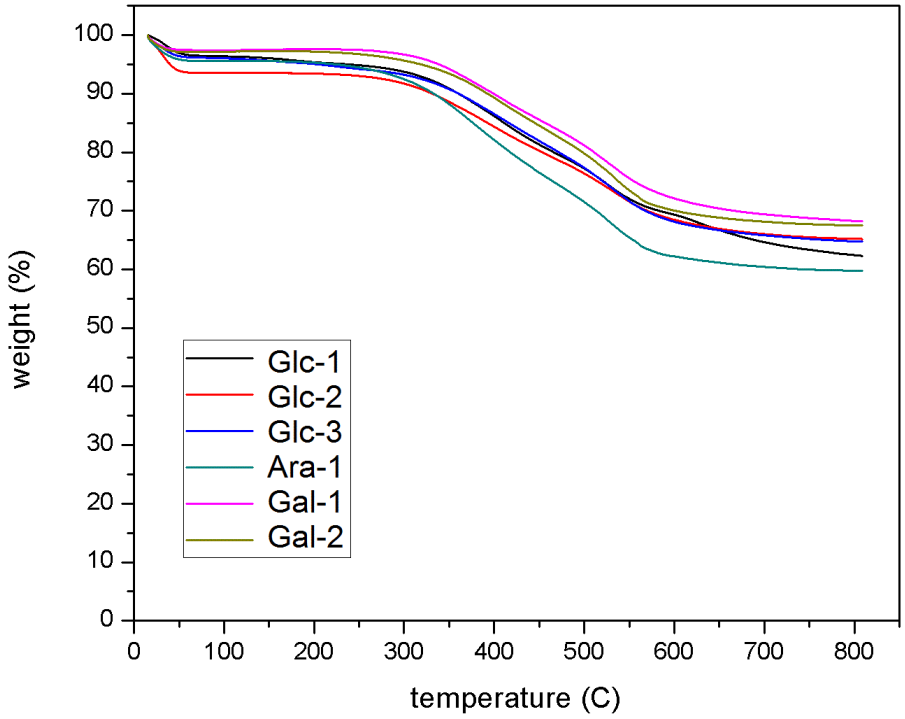


Figure S3. Thermal gravimetric analysis (TGA) analysis of all carbohydrate polymers heated at a rate of 10°C/min up to 900°C under nitrogen flow.

Isothermal adsorption analysis was performed using single gas adsorption isotherms of CO_2 and N_2. The adsorption isotherms were fit using the Toth equation:[S3]

$$n_i^o = \frac{q_{sat} bP}{[1+(bP)^t]^{1/t}}$$

For complete monolayer adsorption coverage, n_i^o is introduced in the modified Langmuir as the amount adsorbed (mmol g^{-1}), q_{sat} for the maximum capacity, b is the temperature dependent affinity parameter, t is fitted as a measure of heterogeneity of the surface, all as a function of pressure (P, kPa). By fitting the isotherms, we can obtain the lnP vs. 1/T at constant loading for each temperature. The slope corresponds to the heat of adsorption, $-\Delta H$ (kJ mol^{-1}), as a function of loading (mmol g^{-1}).

Isotherm fits of absolute loading are used for ideal adsorbed solution theory (IAST) developed by Myers and Prausnitz.[S4] MatLab® was used to calculate the adsorption selectivity from the single gas isotherms of N_2 and CO_2 at a molar ratio of 0.85 : 0.15, respectively.

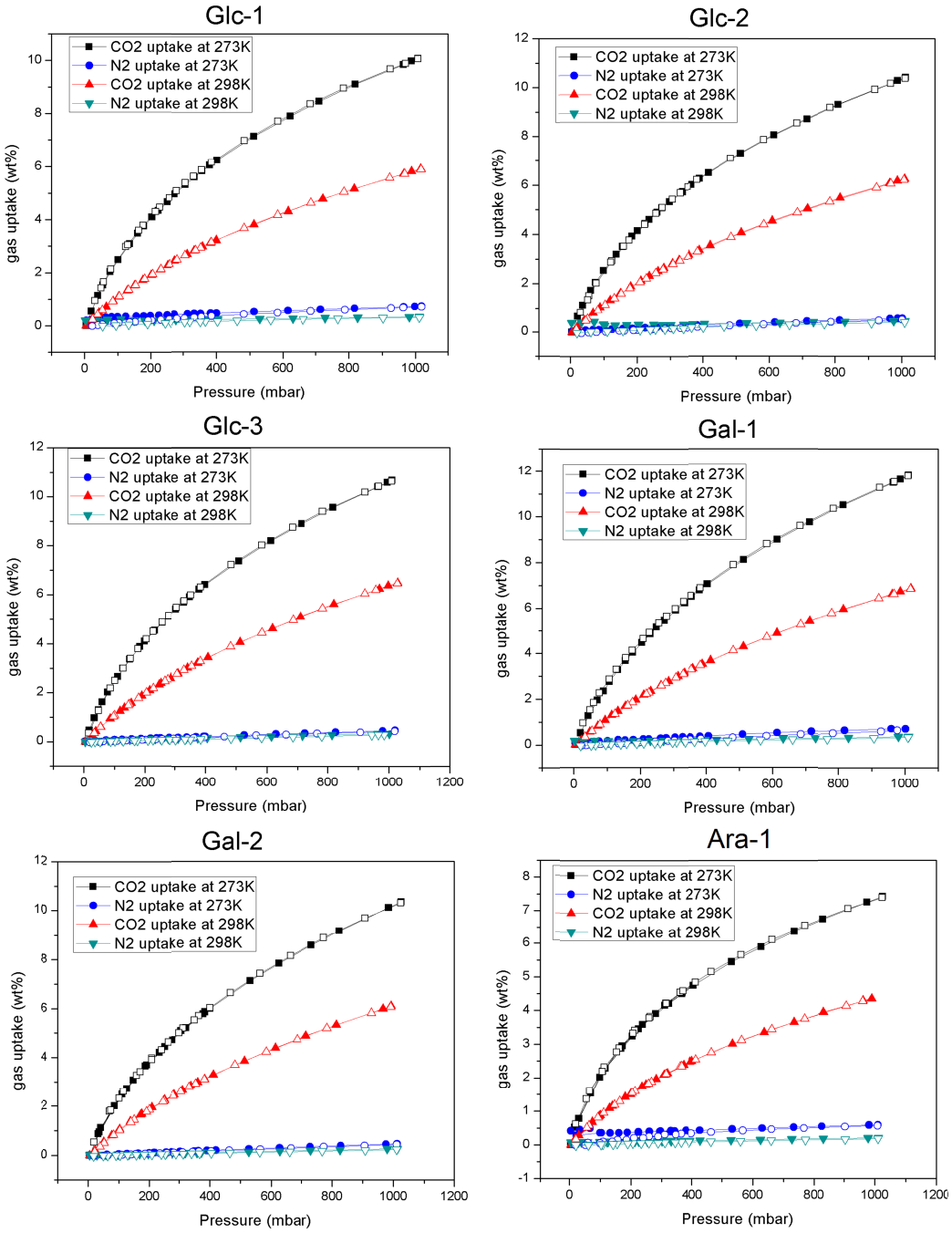


Figure S4. Adsorption (solid symbols) and desorption (open symbols) isotherms of all samples for CO_2 and N_2 at 273 K and 298 K respectively.

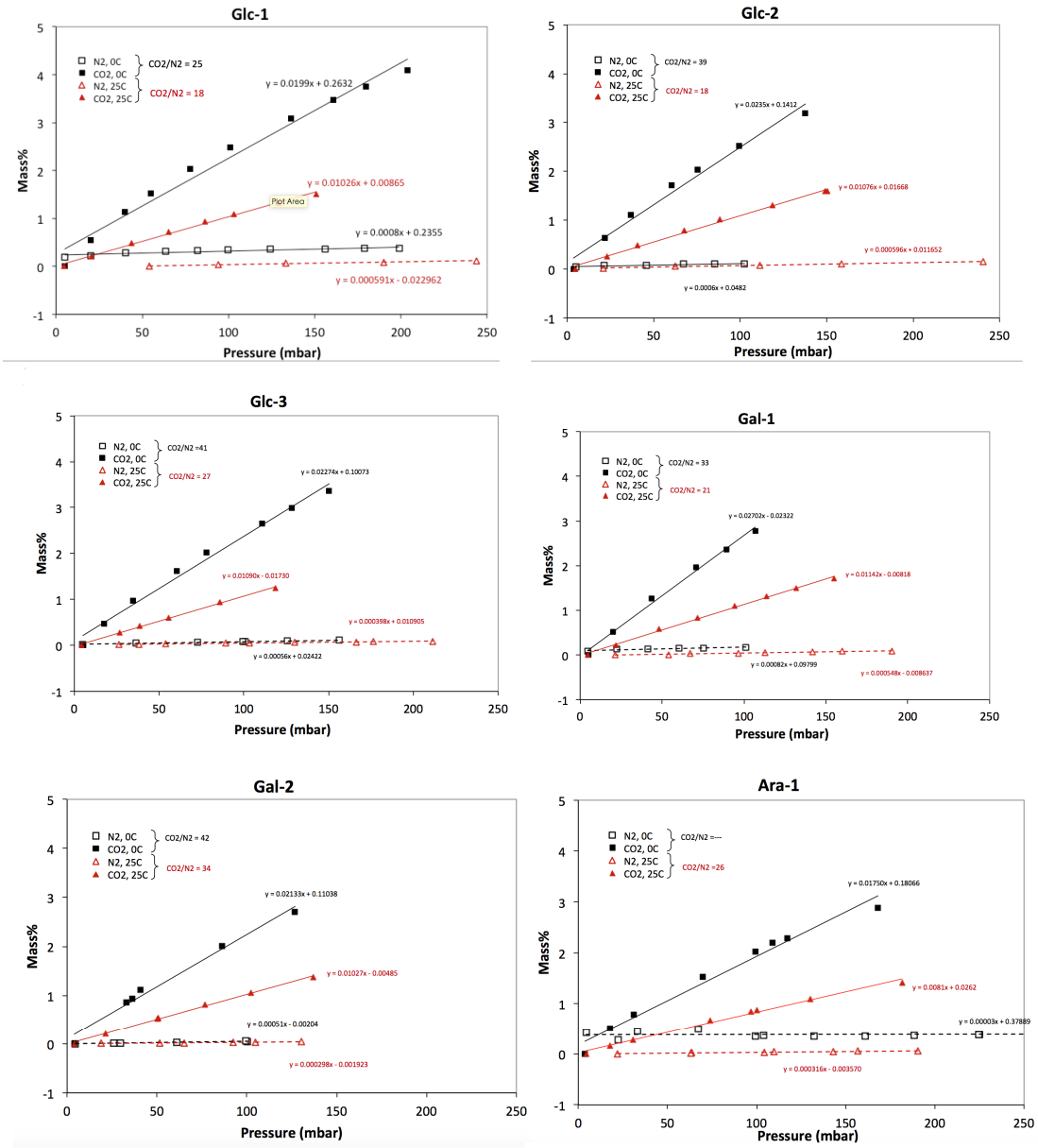


Figure S5. Initial slope calculations for CO_2 and N_2 isotherms collected at 273K and 298 K respectively.

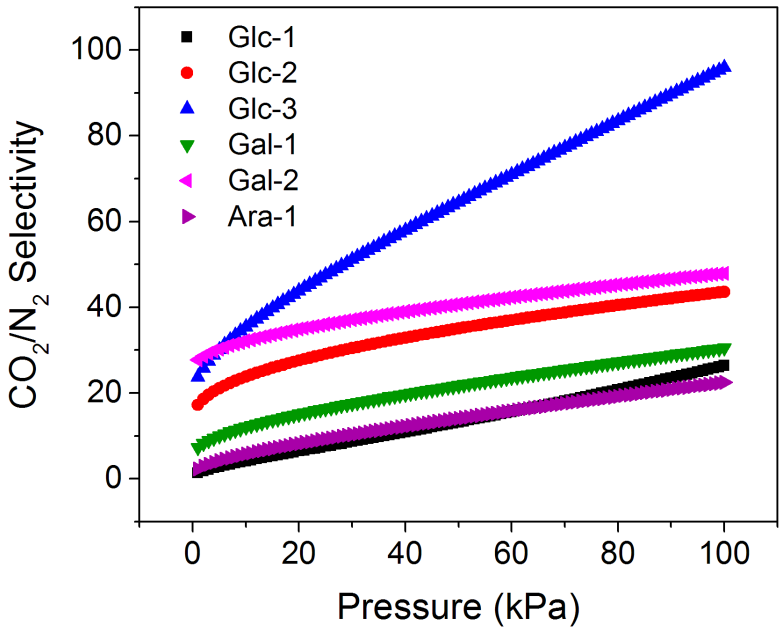


Figure S6. Mixed gas selectivities calculated using the ideal adsorbed solution theory for all samples under 0.15mol CO_2 and 0.85mol N_2 versus pressure.

Table S3. Mixed gas selectivities calculated for all samples under 0.15mol CO_2, 0.85mol N_2 at select pressures.

	Glc-1	Glc-2	Glc-3	Gal-1	Gal-2	Ara-1
Selectivities at 10kPa	4	24	35	12	32	6
Selectivities at 20kPa	6	28	44	15	35	8
Selectivities at 100kPa	26	44	96	31	48	23

Table S4 the comparison of surface area, CO_2 uptake, selectivity (CO_2/N_2) (at 273 and 298 K) and isosteric heat (Qst) in selected POPs with –OH functional groups.

MOP	S_{BET} (m^2g^{-1})	CO_2 uptake (mmol g^{-1})	T (K)	Selectivity	Qst (kJ mol^{-1})	Ref.
Glc-3	829	2.43	273	41	25.8	This work
		1.45	298	27		This work
1-naphthol	414	1.85	273		28-31	S5
		1.25	298	16		S5
1,1-bi-2-naphthol	1015	3.96	273		28-31	S5
		2.27	298	26		S5
phenol	400	2.14	273	-	-	S6
Tetraphenylethylene-HCP	618	1.92	273	119	-	S7
		1.12	298		-	S7

2.Computational details

Quantum chemistry calculations were performed based on DFT method by G09 program. Since

the calculation processes are expensive and time-consuming, basic monomers with simplified structures were applied in the assessment of each type of hyper cross-linked polymers (Figure S6). The geometries of all the monomer and monomer−gas pairs were fully optimized with M062x/6-311g(d, p) method, which is one of the most popular DFT methods in the study of intermolecular interactions. Frequency calculations at the same level were also performed to make sure all optimized structures can represent the actual minimum potential energy. Moreover, all the interaction calculations were corrected with the basis set superposition error (BSSE) by Boys and Bernardi's procedure. In the initial analysis of CO_2−carbohydrate pair systems' geometries, both hydrogen bonding and dipole-quadrupole interactions were considered as initial structures(Figure S7). The binding energy between carbohydrate and gases was calculated by the following formula:

$\Delta E = E(gas-monomer)-E(gas)-E(monomer)+E(BSSE)$.

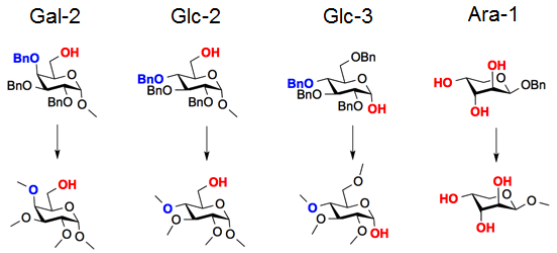


Figure S7. Simplified structures of calculated carbohydrate monomers.

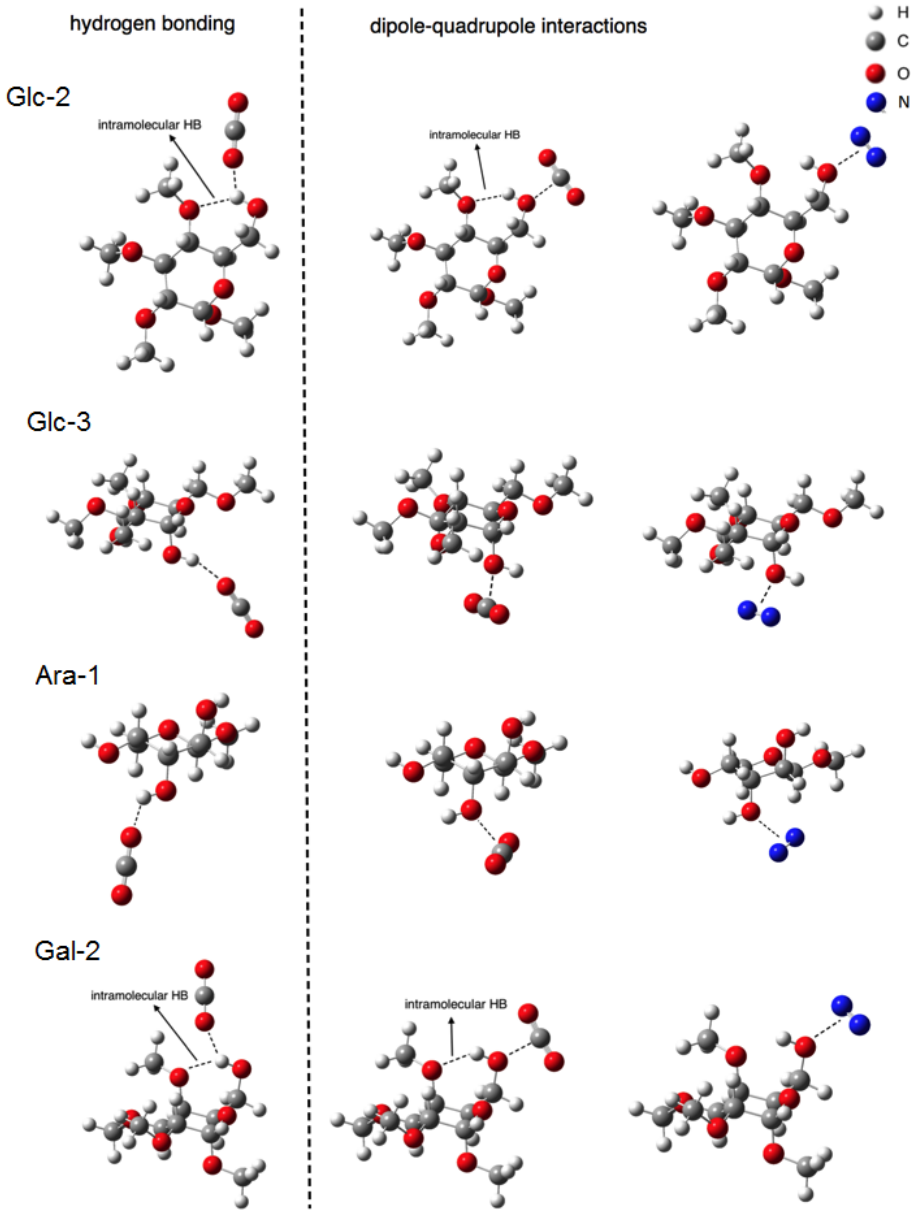


Figure S8. Initial structures of simplified carbohydrate monomer-gas dimer for optimization. All the structures of monomers and gas molecules used for dimer optimization were fully optimized at the same level first.

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S7. S. Yao, X. Yang, M. Yu, Y. Zhang and J. Jiang. J. Mater. Chem. A, 2014, 2, 8054–8059.