Supporting information

For

Synthesis of Glycopolymer Nanosponges with Enhanced Adsorption Performances for Boron Removal and Water Treatment

Xueping Liao,[†][‡] Bingyu Wang,[†][‡] Qiang Zhang[†][‡]^{*}

[†] Jiangsu Key Laboratory of Chemical Pollution Control and Resources Reuse, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China.

[‡] Institute of Polymer Ecomaterials, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China. Email: zhangqiang@njust.edu.cn.

Synthesis of *Heptkis*-(6-deoxy-6-azido)-β-cyclodextrin (β-CD-(N₃)₇)



S Scheme 1. Schematic representation of the synthetic approach to β -CD-(N₃)₇.

Heptkis (6-deoxy-6-bromine)- β -cyclodextrin (β -CD-(Br)₇) was first prepared via a modification of procedures reported by Defaye *et al.*^{1, 2} Ph₃P (18.36 g, 70 mmol) was dissolved in anhydrous DMF (30 mL) under stirring and cooled to 0 °C. NBS (12.46 g, 70 mmol) dissolved in anhydrous DMF (20 mL) was added dropwise to the Ph₃P solution under N₂ atmosphere and then stirred at ambient temperature for 30 min. To a solution of anhydrous β -CD (5.67 g, 5 mmol) in anhydrous DMF (30 mL), the obtained Ph₃P/NBS solution was added dropwise at ambient temperature. The solution temperature was increased to 80 °C after the addition was completed. The mixed brown solution was stirred under N₂ atmosphere for 6 h at 80 °C. After reaction, methanol (10 mL) was added at ambient temperature and stirring was continued for 30 min. The reaction mixture was then cooed to -15 °C and the pH was adjusted to 9 with sodium methoxide, while stirring for further 1 h. The reaction mixture was then poured into stirred ice-water (2 L) resulting the formation of a precipitate which was filtered and washed with MeOH. β -CD-(Br) ₇ (7.08 g, 90%) was obtained as white solids and dried under vacuum for 1 day.

 β -CD-(Br) ₇ (4.73 g, 3 mmol) was then dissolved in anhydrous DMF (40 ml) and NaN₃ (2.73 g, 42 mmol) was added. The resulting suspension was stirred at 70 °C under N₂ atmosphere for 48 h. The suspension was then concentrated under reduced pressure before precipitation into large excess of water. The precipitate was filtered and washed with water. The obtained white powder (3.72g, 95%) was dried under vacuum at ambient temperature for 24 h.

¹H NMR (DMSO- d_6 , 298 K, 500 MHz): δ =5.89 (d, J=6.8 Hz, 7 H, OH-2), 5.75 (d, J=1.7 Hz, 7 H, OH-3), 4.91(d, J=3.3 Hz, 7 H, H-1), 3.67-3.86 (m, 14 H, H-6a, H-5), 3.50-3.66 (m, 14 H, H-3, H-6b), 3.26-3.44 (m, 14 H, H-2, H-4, overlap with H₂O) ppm.

¹³C NMR (DMSO-*d*₆, 298 K, 125 MHz): δ =102.1 (C-1), 83.2 (C-4), 72.6 (C-3), 72.0(C-2), 70.3(C-5), 51.3 (C-6) ppm.

FT-IR v: 3334(OH); 2922 (CH); 2098 (N₃) cm⁻¹.

Preparation of H₂SO₄-silica catalyst

 H_2SO_4 -silica catalyst was prepared according to the literature procedure.³ To a mixture of silica gel (10 g, 200–400 mesh) in diethyl ether (50 mL), commercially available concentrated H_2SO_4 (3 mL) was added slowly with shaking for 15 min. The solvent was then evaporated under reduced pressure resulting in free flowing H_2SO_4 -silica catalyst, which was then dried at 110 °C for 3 h.

Synthesis of alkyne-functionalized pyranose / furanose

1-(2'-propargyl) D-glucose, 1-(2'-propargyl) D-mannose, 1-(2'-propargyl) *N*-Acetyl-D-glucosamine and 1-(2'-propargyl) D-Ribose were prepared according to procedures described in previous literature.^{3, 4} Typically, a suspension solution of monosaccharide (e.g., D-(-)-ribose, 15.01 g, 100 mmol), propargyl alcohol (29.1 mL, 500 mmol) and H₂SO₄-silica (500 mg) was stirred at 65 °C until all the reagents completely dissolved (~ 2.5 h) and the reaction was allowed for further 5 h. After cooling to ambient temperature, the solution was directly transferred to a silica gel column for purification using DCM-MeOH (8:1) as the eluent to remove the unreacted propargyl alcohol and D-(-)-ribose. The final product was obtained as light yellow solid (yield: 30 %) after drying under vacuum. The product as an anomeric mixture was used directly for the next step reaction. ESI-MS spectrum confirmed the presence of targeted products at 211.01 (calcd for $m/z C_8H_{12}O_5Na^+$ (M + Na), 211.07).

For detailed characterisation, a part of the product was per-O-acetylated using acetic anhydride. A suspension solution of 1-(2'-propargyl) D-Ribose (188 mg, 1.00 mmol), acetic anhydride (3.0 mL, 32.0 mmol), H₂SO₄-silica (6 mg) was stirred at ambient temperature for 48 h. After completion of the reaction, the solution was diluted with DCM (20 mL) and washed sequentially with saturated aq. NaHCO₃ solution and water twice. The extract was dried over MgSO₄ and concentrated under vacuum. However, TLC (petroleum ether: ethyl acetate =4: 1) confirmed the presence of two very close spots (R_f value = ~ 0.3), however, silica gel column chromatography was not able to separate this anomeric mixture. Sample was then taken for ¹H NMR and FTIR spectroscopy (Figure S 2; Figure S 3) to confirm the anomeric ratio in the mixture and targeted alkyne groups.



Figure S 1. TGA analysis of different GNs



Figure S 2. ¹H NMR spectrum of per-O-acetylated 1-(2'-propargyl) D-ribose in CDCl₃.



Figure S 3. FTIR spectra of D-(-)-ribose and 1-(2'-propargyl) D-ribose.



Figure S 4. FTIR spectra of *N*-(prop-2-yn-1-yl) D-Gluconamide.





Figure S 5. FTIR spectra of functional GNs.



Figure S 6. N₂ adsorption (blue) / desorption (red) isotherms and pore volume *vs* pore diameter (inset) for poly(β -CD) (**top**), poly(β -CD)-*co*-(β -CD-(N₃)₇) (**middle**) and poly(β -CD)-*co*-(β -CD-(N₃)₇) (**@** Mannose (**bottom**). S_{BET} is the Brunauer–Emmett–Teller (BET) surface area (in units of m²/g) calculated from the N₂ adsorption isotherm; P and P₀ are the equilibrium and saturation pressures of N₂ at 77 K, respectively. The Barret–Joyner–Halenda (BJH) method was used to estimate the pore volume and pore diameter from the adsorption isotherm.

GNs Adsobents	$Q_{\rm e}^{a}({ m mg} / { m g})$	pseudo-first-order model			pseudo-second-order model		
		$Q_{\rm cal}{}^b({ m mg}/{ m g})$	k_1^{c} (h ⁻¹)	<i>R</i> ²	$Q_{\mathrm{cal}}{}^{d}$ (mg / g)	k_2^{e} (g / mg · h)	R ²
poly(β-CD)-co-(β-CD-(N ₃) ₇)@Ribose	19.60	8.43	0.099	0.5208	19.66	0.050	0.988
poly(β-CD-(N ₃) ₇)@Gluconolactone	32.36	12.13	0.265	0.8828	33.00	0.058	0.999

Table S 1. Fitting Parameters for Boron Adsorption Kinetics by Pseudo-first Order and Pseudo-second Order Models to GNs Adsorbents.

a Equilibrium sorbed concentration from the experiment at initial concentration of boron 300 mg / L and pH 9.2.

^b Calculated equilibrium sorbed concentration from the pseudo-first-order model.

^{*c*} Rate constant for pseudo-first-order model.

^d Calculated equilibrium sorbed concentration from the pseudo-second-order model.

^{*e*} Rate constant for the pseudo-second-order model.

Table S 2. Freundlich Model Parameters (K_F and $n \pm$ Standard Deviation) and Langmuir Model Parameters (K_L and $Q_{max} \pm$ Standard Deviation)for MB (initial concentration 400 mg / L) Adsorption to Different GNs Adsorbents.

GNs Adsorbents		Freundlich		Langmuir			
	К _F (mg ¹⁻ⁿ L ⁿ / g)	n	<i>R</i> ²	<i>К</i> _L (L / mg)	<i>Q</i> _{max} (mg / g)	<i>R</i> ²	
poly(β-CD)	252.1±26.7	0.26±0.02	0.992	0.0863±0.0557	1138.9±145	0.851	
poly(β-CD-(N ₃) ₇)	147.3±26.6	0.24±0.03	0.963	0.0331±0.0179	710.6±74.9	0.779	
$poly(\beta-CD)-co-(\beta-CD-(N_3)_7)$	187.7±52.2	0.33±0.05	0.958	0.0218±0.0110	1587.1±198.3	0.890	
$poly(\beta-CD)-co-(\beta-CD-(N_3)_7)@Mannose$	348.4±43.8	0.17±0.02	0.967	0.1438±0.0477	898.2±49.9	0.932	

Adsorbent	Dye	Q _{max} (mg / g)	Reference
GNS/β-CD composite	MB	580.4	5
β -CD /p oly(acrylic acid)/grapheme oxide nanocomposites	MB	248	6
Magnetic B-CD grafted carbon nanotube composites	MB	196.5	7
β-CD -based electrospun fiber	MB	826.5	8
Sericin/β-CD /PVA composite electrospun nanofibers	MB	187.3	9
CD/silics hybrid adsorbent	MB	212	10
Carbourmethyl & CD medified meanatic nene adapthent	MD	212	11
Carboxymethyl-p-CD modified magnetic nano adsorbent	MB	277.8	10
B-CD/carboxymethyl cellulose polymer	MB	56.5	10
β-CD polymer crosslinked by citric acid	MB	105	12
Rhamnolipid-functionalized graphene oxide	MB	529.1	13
Activated carbon	MB	521	14
Alkali-activated Palygorskite	MB	154.6	15

Table S 3. MB adsorption capacity of different adsorbents as reported in the literatures. .

Table S 4. Fitting Parameters for MB Adsorption Kinetics by Pseudo-first Order and Pseudo-second Order Models to GNs Adsorbents.

GNs Adsorbents	$Q_{e^{a}} (mg / g)$	pseudo-first-order model			pseudo-second-order model		
		Q_{cal}^{b} (mg / g)	k_1^c (h ⁻¹)	<i>R</i> ²	$Q_{\mathrm{cal}^d} (\mathrm{mg}/\mathrm{g})$	k_2^e (g / mg · h)	<i>R</i> ²
poly(β-CD)	848.0	489.8	0.055	0.8735	833.3	0.554×10-3	0.984
poly(β-CD-(N ₃) ₇)	601.2	326.4	0.125	0.8828	625.0	1.164×10-3	0.997
poly(β-CD)-co-(β-CD-(N ₃) ₇)	781.1	413.3	0.057	0.927	769.2	0.704×10 ⁻³	0.989
poly(β-CD)-co-(β-CD-(N ₃) ₇)@Mannose	811.0	211.3	0.032	0.677	769.2	1.536×10-3	0.994
poly(β-CD)-co-(β-CD-(N ₃) ₇)@Glucosamine	1027.5	219.5	0.061	0.814	1000	2.000×10-3	0.999
poly(β-CD-(N ₃) ₇)@Gluconolactone	704.1	189.6	0.050	0.797	714.3	1.782×10-3	0.997
poly(β-CD-(N ₃) ₇)@Glucosamine	579.5	169.0	0.046	0.739	588.2	1.806×10-3	0.995

^a Equilibrium sorbed concentration from the experiment at initial concentration of MB 400 mg / L and pH 6.8.

^b Calculated equilibrium sorbed concentration from the pseudo-first-order model.

^c Rate constant for pseudo-first-order model.

^d Calculated equilibrium sorbed concentration from the pseudo-second-order model.

^{*e*} Rate constant for the pseudo-second-order model.

References

- 1. K. Chmurski and J. Defaye, *Supramolecular Chemistry*, 2000, **12**, 221-224.
- 2. Q. Zhang, L. Su, J. Collins, G. Chen, R. Wallis, D. A. Mitchell, D. M. Haddleton and C. R. Becer, J. Am. Chem. Soc., 2014, 136, 4325-4332.
- 3. B. Roy and B. Mukhopadhyay, *Tetrahedron Lett*, 2007, 48, 3783-3787.
- 4. Q. Zhang, S. Slavin, M. W. Jones, A. J. Haddleton and D. M. Haddleton, *Polym. Chem.*, 2012, **3**, 1016-1023.
- 5. P. Tan and Y. Hu, *Journal of Molecular Liquids*, 2017, **242**, 181-189.
- 6. J. Liu, G. Liu and W. Liu, *Chem. Eng. J.*, 2014, **257**, 299-308.
- 7. J. Cheng, P. R. Chang, P. Zheng and X. Ma, *Industrial & Engineering Chemistry Research*, 2014, **53**, 1415-1421.
- 8. R. Zhao, Y. Wang, X. Li, B. Sun and C. Wang, *ACS applied materials & interfaces*, 2015, 7, 26649-26657.
- 9. R. Zhao, Y. Wang, X. Li, B. Sun, Z. Jiang and C. Wang, *Colloids and surfaces. B, Biointerfaces*, 2015, **136**, 375-382.
- 10. L. B. d. Carvalho, T. G. Carvalho, Z. M. Magriotis, T. d. C. Ramalho and L. d. M. A. Pinto, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, 2012, **78**, 77-87.
- 11. A. Z. M. Badruddoza, G. S. S. Hazel, K. Hidajat and M. S. Uddin, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2010, **367**, 85-95.
- 12. D. Zhao, L. Zhao, C.-S. Zhu, W.-Q. Huang and J.-L. Hu, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, 2009, **63**, 195-201.
- 13. Z. Wu, H. Zhong, X. Yuan, H. Wang, L. Wang, X. Chen, G. Zeng and Y. Wu, *Water research*, 2014, **67**, 330-344.
- 14. R. Y. Hong, B. Feng, G. Liu, S. Wang, H. Z. Li, J. M. Ding, Y. Zheng and D. G. Wei, *Journal of Alloys and Compounds*, 2009, **476**, 612-618.
- 15. W. Wang, F. Wang, Y. Kang and A. Wang, *Water, Air, & Soil Pollution*, 2015, 226.