

# Novel Chemical Architectures Based on Beta-Cyclodextrin Derivatives Covalently Attached on Polymer Spheres

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## Ts-BCD

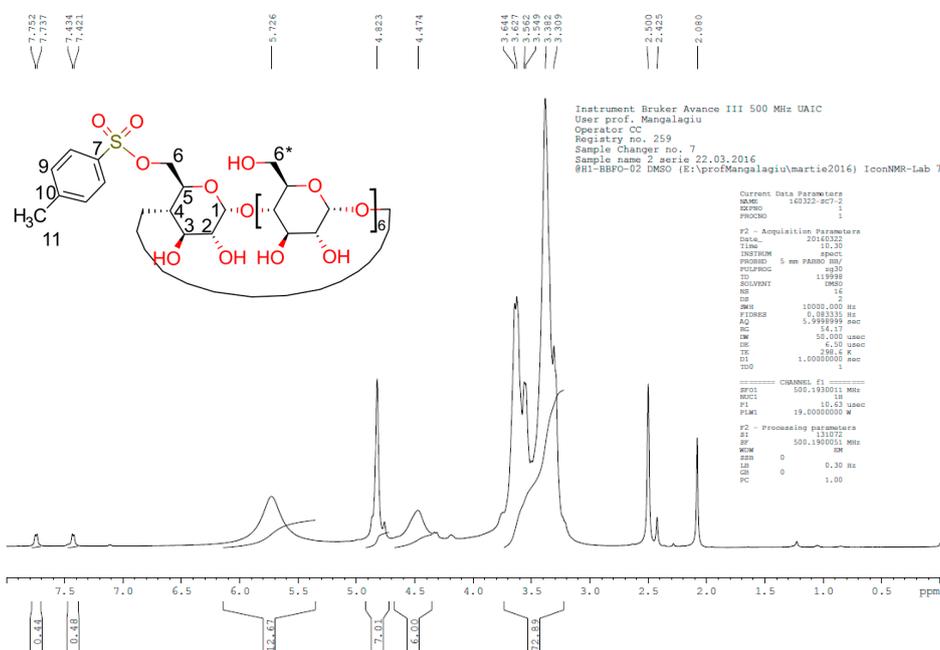


Figure S1. <sup>1</sup>H-NMR spectrum Ts-BCD

Data: I2 blank 1075Da op1311Da0001.2I2[c] 18 Dec 2015 12:35 Cal: tof 25 Nov 2014 14:34  
 Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron\_HiRes, Power: 60, Blanked, P.Ext. @ 1311 (bin 73)

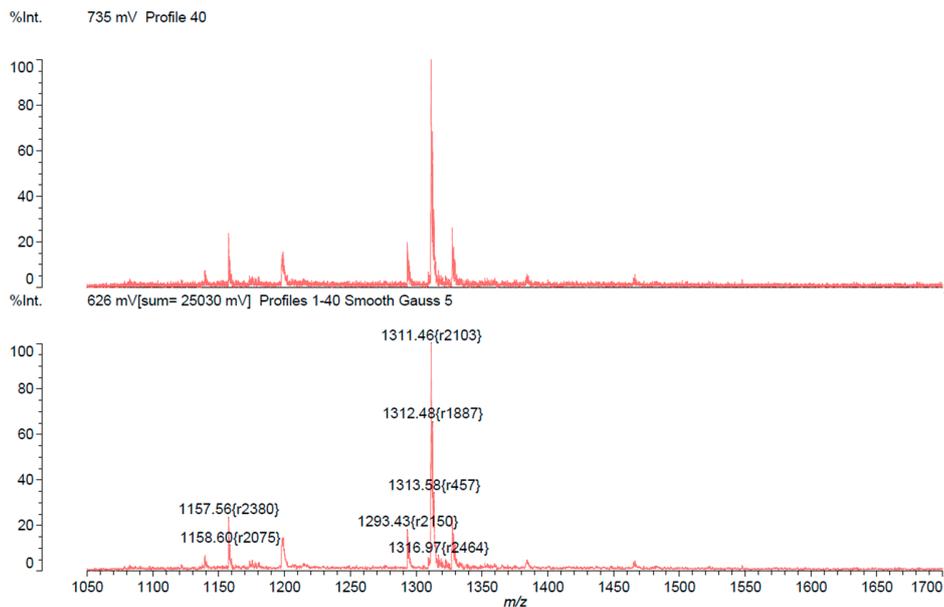


Figure S2. MALDI-TOF results for BCD-Ts

BCD-NH<sub>2</sub>

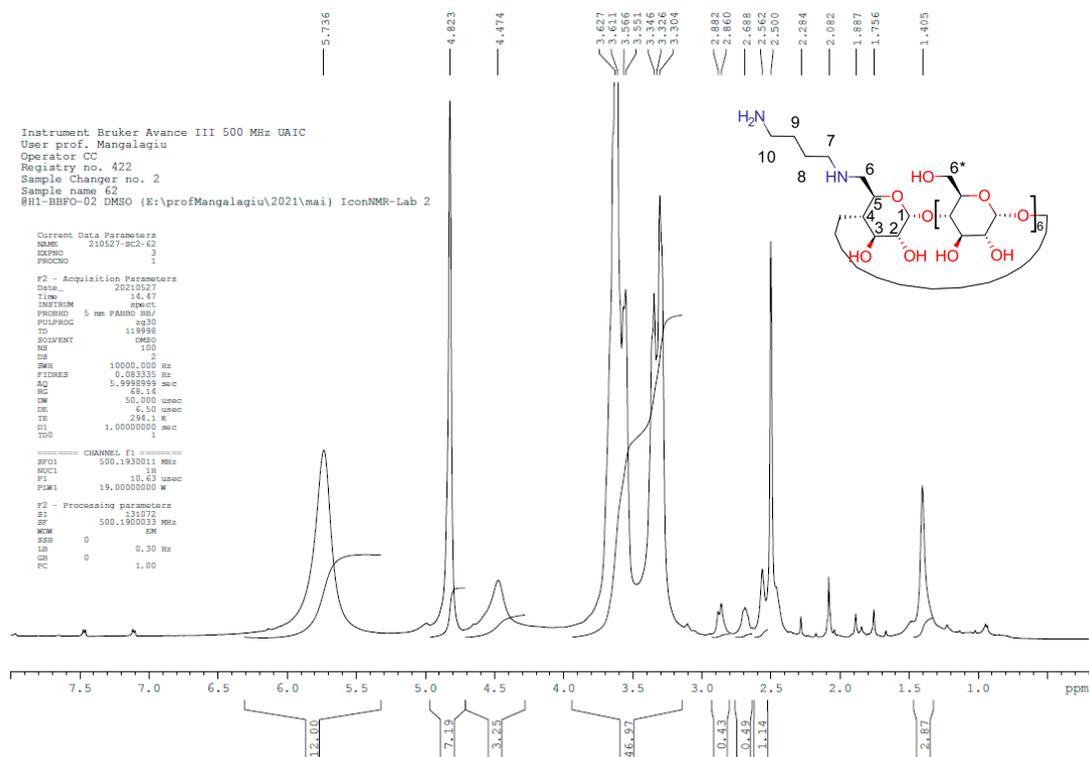


Figure S3. <sup>1</sup>H-NMR spectrum diamino butane-BCD (BCD-NH<sub>2</sub>)

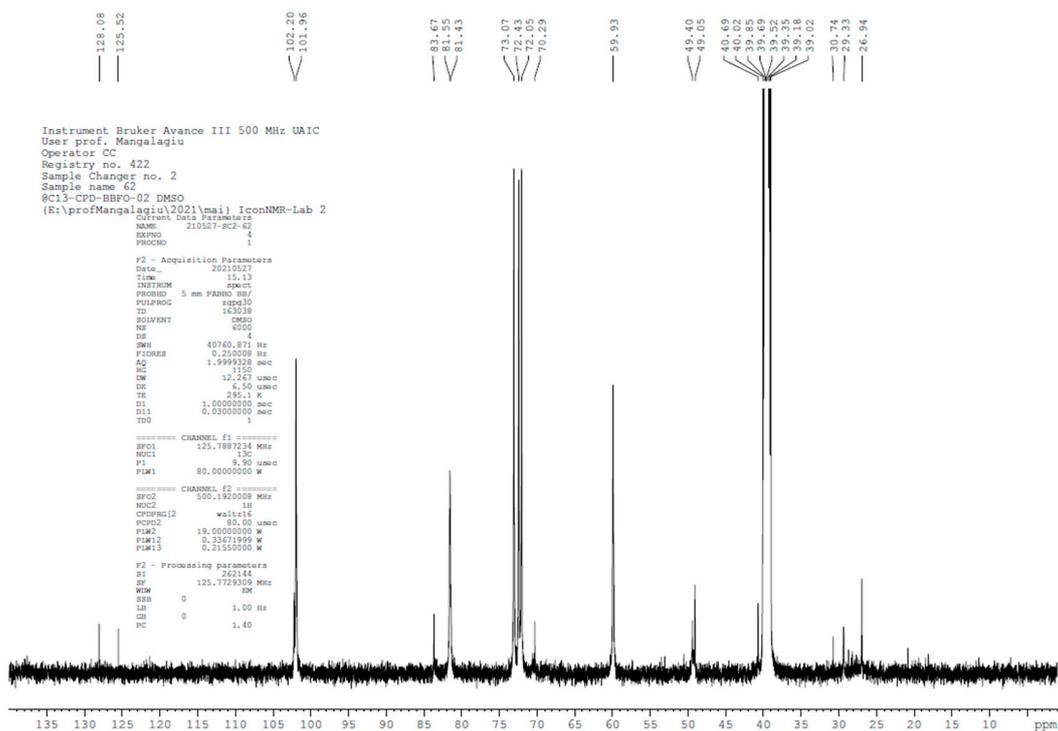


Figure S4. <sup>13</sup>C-NMR spectrum diamino butane-BCD (BCD-NH<sub>2</sub>)

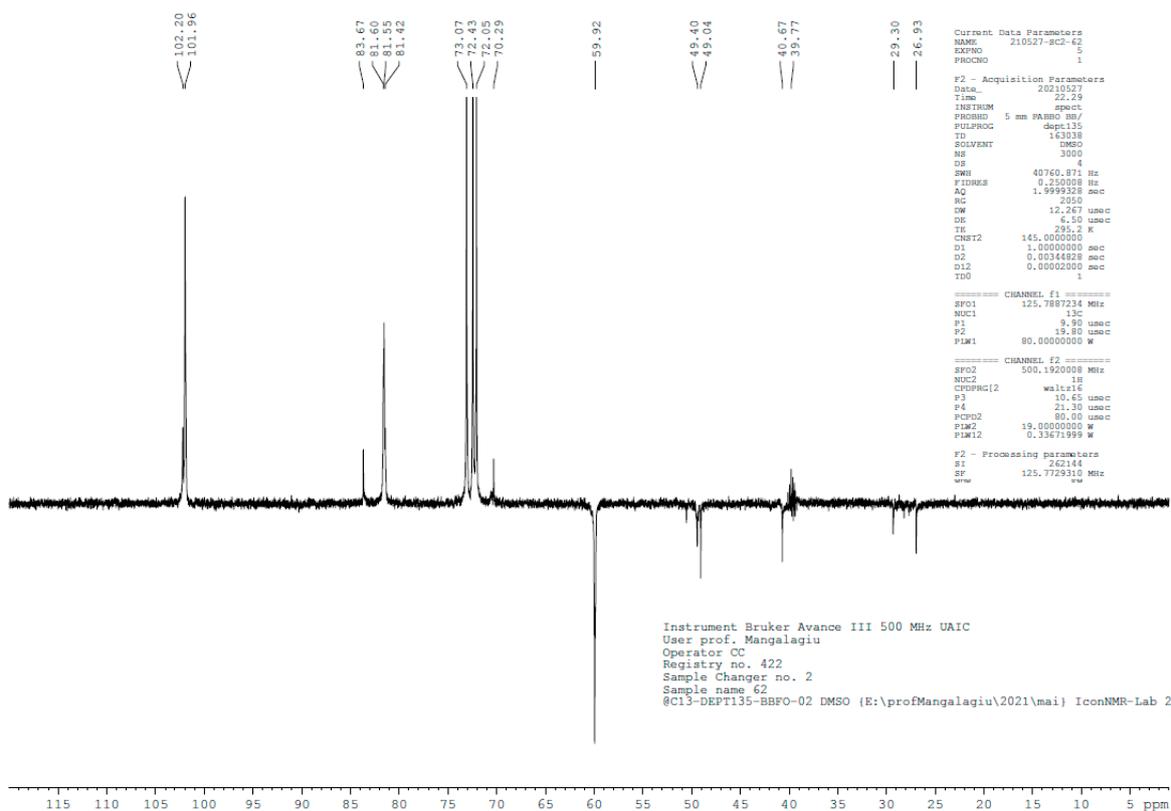


Figure S5. DEPT NMR spectrum diamino butane-BCD (BCD-NH<sub>2</sub>)

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Instrument Bruker Avance III 500 MHz UAIC
User prof. Mangalagiu
Operator CC
Registry no. 422
Sample Changer no. 2
Sample name 62
@HMCCgs-BBFO-02 DMSO
{E:\profMangalagiu\2021\mai} IconNMR-Lab 2

Current Data Parameters
NAME 210527-sc2-62
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210527
Time 22.31
INSTRUM spect
PROBHD 5 mm PARAS HNP
PULPROG hmqcpgpgf
TD 1024
SOLVENT DMSO
NS 8
DS 16
SHE 836.722 Hz
FIDRES 8.004611 Hz
AQ 0.0424440 sec
RG 2050
DM 61.000 usec
DE 4.10 usec
TE 294.2 K
CH2F2 145.000000 sec
D0 0.00000000 sec
D1 1.50000000 sec
D2 0.00344828 sec
D12 0.00000000 sec
D13 0.00000400 sec
D14 0.00000000 sec
IND 0.00001590 sec

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SFO1 500.133013 MHz
NUC1 1H
P1 10.62 usec
P2 71.24 usec
PLW1 19.00000000 W

===== CHANNEL f2 =====
SFO2 125.767399 MHz
NUC2 13C
CPDPRG2 gmc
P3 9.90 usec
P4 70.00 usec
PLW2 80.00000000 W
PLW3 1.40000000 W

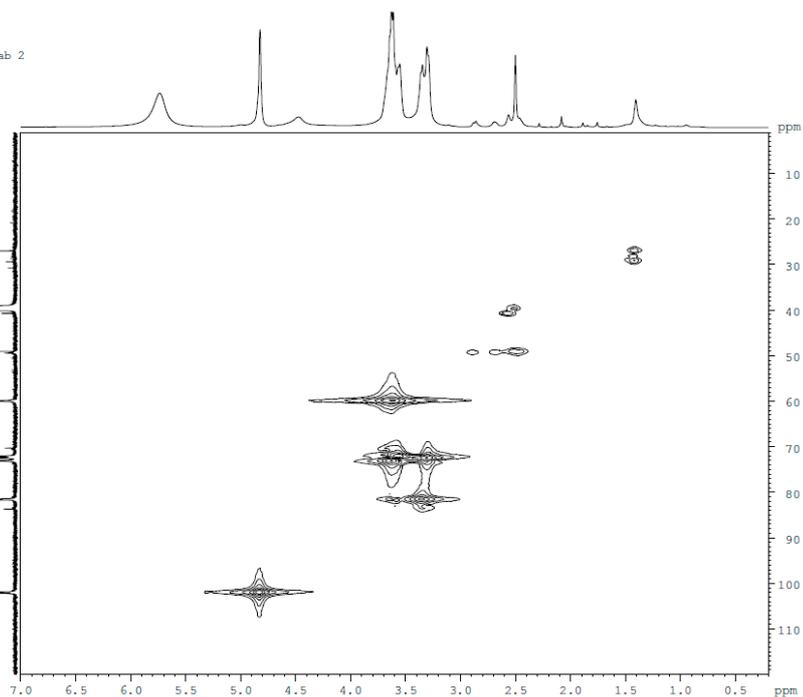
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GPR1 50.00 %
GPR2 30.00 %
GPR3 40.10 %
GPR4 1000.00 usec

F1 - Acquisition parameters
TD 256
SFO1 125.7673 MHz
FIDRES 122.839051 Hz
SW 249.998 ppm
FAMODE GF

F2 - Processing parameters
SI 1024
SF 500.130033 MHz
WDW QDRNG
SSB 0 Hz
GB 0
PC 1.60

F1 - Processing parameters
SI 1024
WDW

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**Figure S6. HMQC NMR spectra diamino butane-BCD (BCD-NH<sub>2</sub>)**

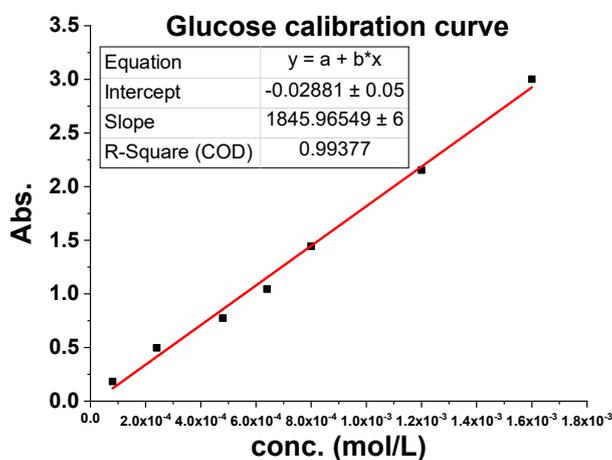
### Determination of cyclodextrin content in the polymer

The  $\beta$ -cyclodextrin content was quantified by determining the reducing sugars of the polymer using concentrated H<sub>2</sub>SO<sub>4</sub> acidolysis and phenol colorimetric analysis [1]. First, the method requires the preparation of a calibration curve. The solutions containing various concentrations of anhydrous glucose were mixed with 1 mL of 4% phenol standard solution and 7 mL of concentrated sulfuric acid. After vigorous shaking, the solutions were incubated at 50°C for 30 minutes and then the absorbance of the aqueous mixture was measured at room temperature. The absorbance values at 490 nm were plotted versus the concentration of anhydrous glucose to obtain the calibration curve.

The polymer analysis procedure involves the dispersing of 10 mg polymer (ST-HEMA-GMA-BCD-OH or ST-HEMA-GMA-BCD-NH<sub>2</sub>) in 2 mL H<sub>2</sub>O. After, 7 mL of concentrated sulfuric acid and 1 mL of 4% phenol standard solution were added and the solution was incubated at 80°C to ensure hydrolysis and phenol coupling reaction. The glucose level was assessed using the calibration curve and the BCD content was calculated as follows:

$$BCD \text{ content} = \frac{c \times V \times M}{180 \times n \times 0.01} \times 100 \%$$

Where 180 is the molecular weight of glucose,  $c$  is the glucose concentration (g/L);  $V$  is the volume of mixed solution (L);  $M$  is the molar mass of BCD (g/mol); 180 is the molecular weight of glucose, 0.01 are the grams of sample and  $n$  is the number of glucoses in a BCD unit.



**Figure S7. Glucose calibration curve (Abs. 490 nm vs glucose concentration)**

#### **Adsorption studies of bisphenol A - quantification by fluorescence spectroscopy**

The adsorption of bisphenol A onto BCD substituted polymer particles ST-HEMA-GMA-BCD-OH and ST-HEMA-GMA-BCD-NH<sub>2</sub> was conducted using batch equilibrium technology in a mixed solution of ethanol and doubly distilled water (v:v 3:7) at the desired concentrations and a pH value of 5. In general, 0.01 g of polymer particles were dispersed thoroughly in a 50 mL solution of bisphenol A at various concentrations (5–30 mg/ L) and shaken in a thermostatic bath (shaker operated at a speed of 180 rpm at 25 °C). After equilibrium was reached, the solid sample was separated by centrifugation. The concentration of bisphenol A in the residual solution was determined using fluorescence spectrophotometry (bisphenol A:  $\lambda_{ex}/\lambda_{em}$  274/307)

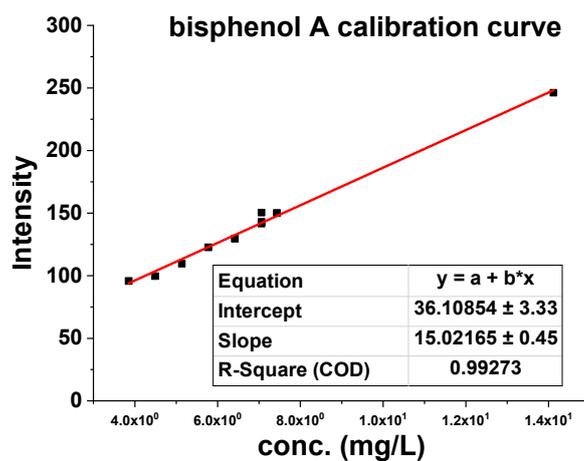


Figure S8. Plot of calibration curve for bisphenol A solution with different concentrations

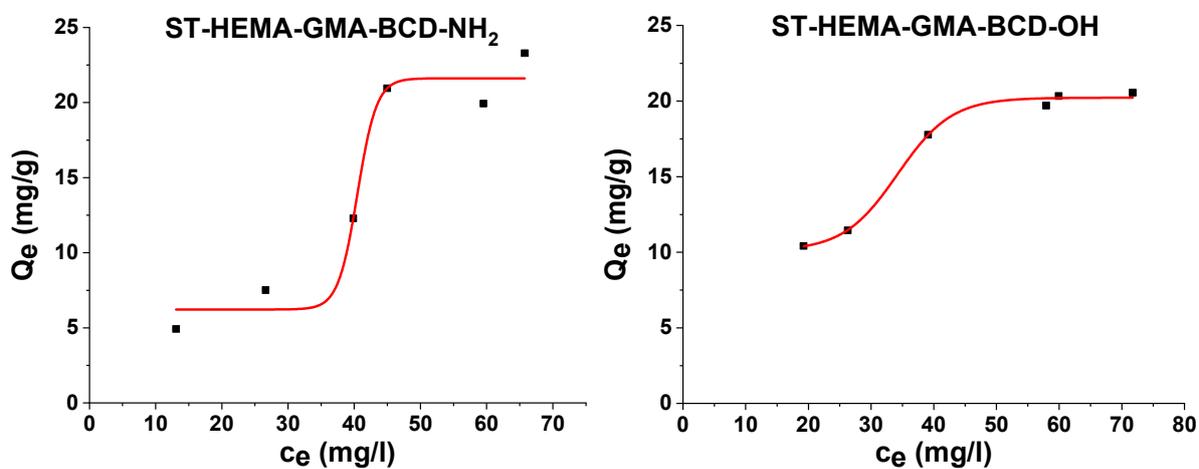


Figure S9. Equilibrium isotherms for bisphenol A at 25°C in the case of ST-HEMA-BCD-NH<sub>2</sub> and ST-HEMA-BCD-OH

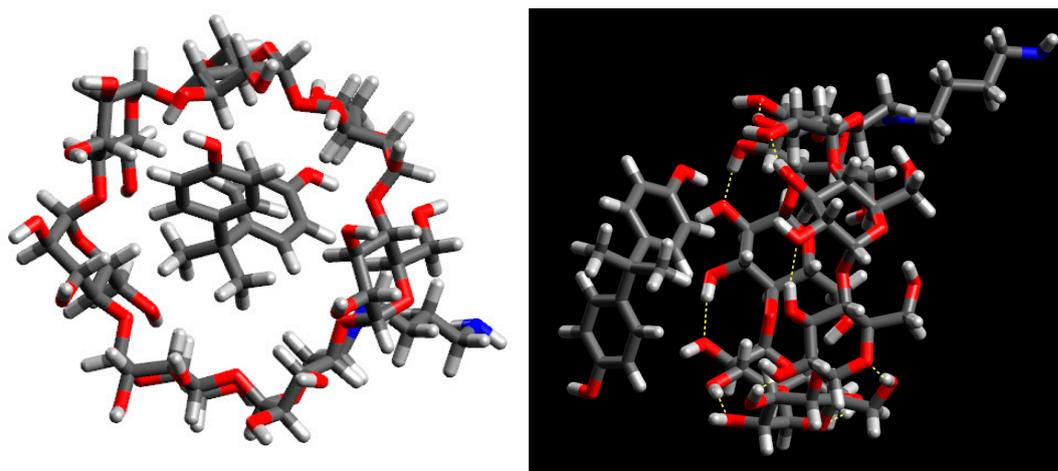
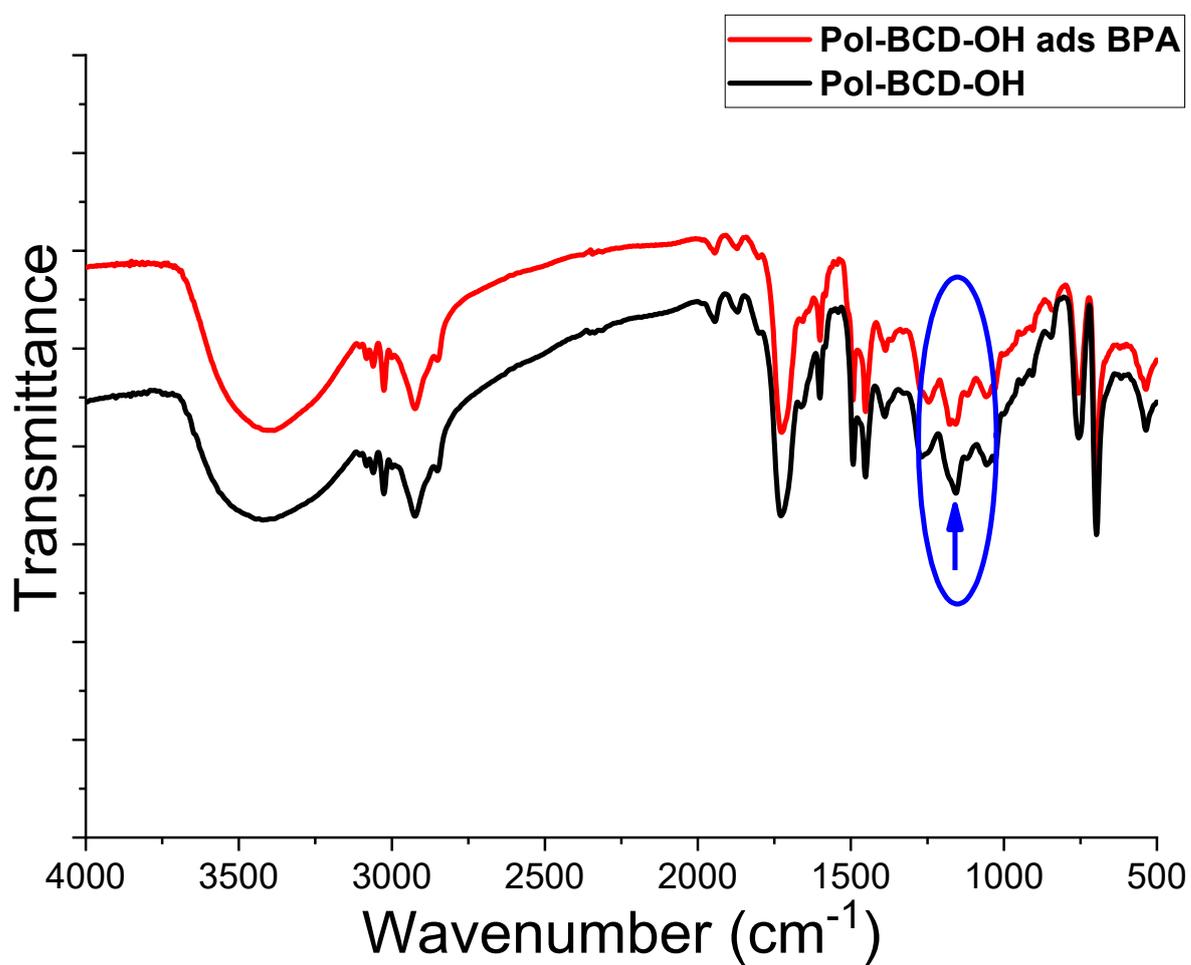
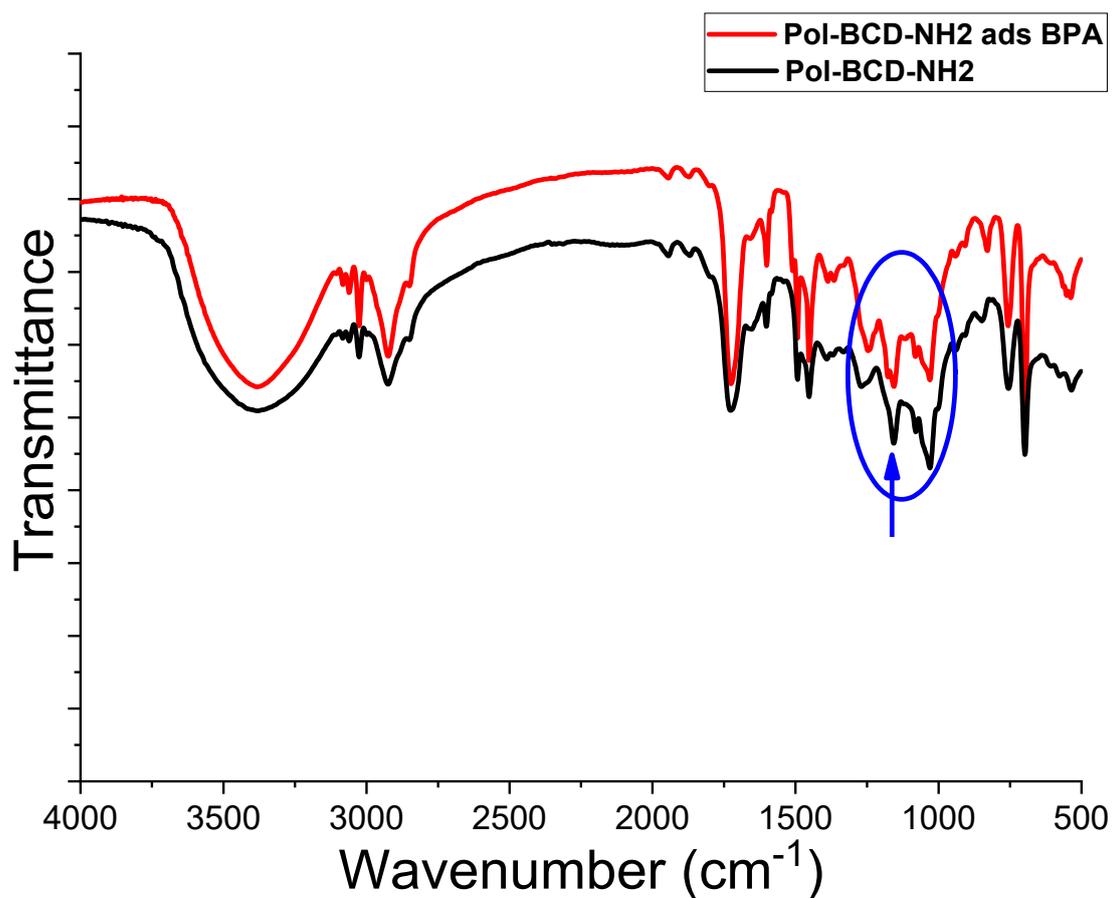


Figure S10. 3D rendering of bisphenol A insertion in BCD-NH<sub>2</sub>



a)



**Figure S11. FT-IR spectra of the polymer materials modified with BCD derivatives after BPA adsorption study**

#### Reference

1. DuBois, M.; Gilles, K.A.; Hamilton, J.K.; Rebers, P.A.; Smith, F. Colorimetric Method for Determination of Sugars and Related Substances. *Anal. Chem.* **1956**, *28*, 350-356, doi:10.1021/ac60111a017.