

Electronic Supplementary Information

Modification of Cellulose Nanocrystal Surface Chemistry with Diverse Nucleophiles for Materials Integration

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Instrumentation:

AFM data were taken using a Bruker Dimension ICON Atomic Force Microscope in tapping mode controlled by Nanoscope software using a Bruker RTESP-150 (resonance frequency = 150 kHz; S-3 force constant = 6.0 N m^{-1}) AFM Probe. Height and width profiles were measured with Gwyddion 2.50 software.

Dynamic Light Scattering (DLS) was performed with a Wyatt DynaPro NanoStar at 25°C in a quartz cuvette in an aqueous solution containing 3.8% DMF.

X-ray Diffraction (XRD) was performed to obtain the crystal structure and percent crystallinity of the CNCs. This was done using a Panalytical X'Pert Pro Alpha-1 XRD operated at 40 mA. The range of scanned angles was 5° to 35° using a $1/4^\circ$ anti-scatter slit and a 0.04 radian soller slit.

Zeta potential was measured with a Malvern Zetasizer Nano Z at 25°C .

CNCs were homogenized using an IKA T25 digital ULTRA TURRAX disperser and freeze-dried using a Labconco FreeZone 4.5 lyophilizer.

IR spectroscopy was run on a Shimadzu Prestige 21 FT-IR. ^{13}C CP/MAS experiments were performed on a 300 Hz Bruker AV3 HD NMR spectrometer for 2k scans.

Elemental analysis (EA) was performed by Atlantic Microlab, Inc in Norcross, Georgia.

Sessile water contact angles were measured using a Rame-Hart Inc. model 300 goniometer. CNC samples were pressed into 50-60 mg 13-mm pellets with 2000 psi of pressure to ensure a smooth surface.

Size of CNCs:

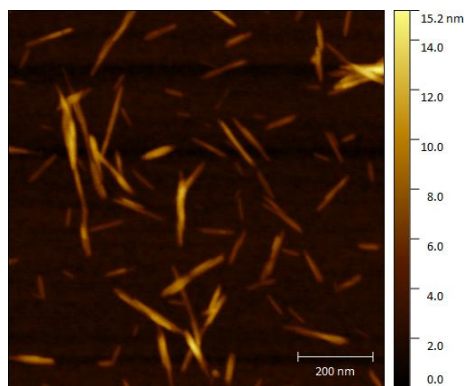
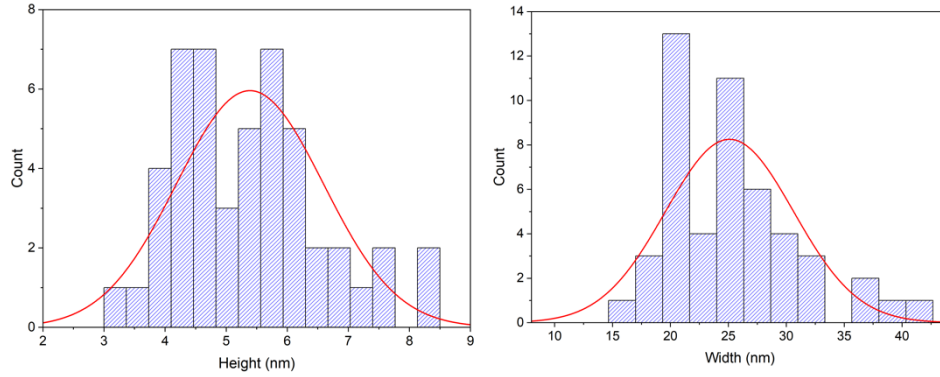


Figure S1: AFM image of unmodified CNCs dispersed on a silica wafer.



$$h = 5.43 \pm 1.17 \text{ nm}$$

$$w = 24.10 \pm 5.53 \text{ nm}$$

Figure S2: (a) Height and (b) width profiles from 50 CNC particles taken from AFM images.

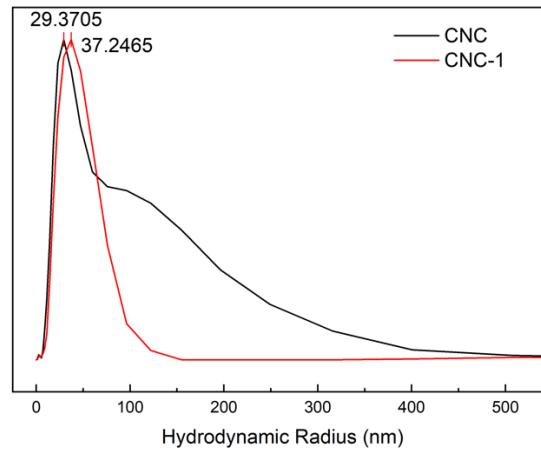


Figure S3: DLS particle size distribution of unmodified CNCs (black) and **CNC-1** (red) in a 3.8% H₂O in DMF solution. Peak labeled hydrodynamic radius (R_h)

Calculation of unmodified CNC length from the average hydrodynamic radius (R_h) found from DLS. ¹

$$R_h = 29.37 \text{ nm} = \frac{L}{2 \ln\left(\frac{L}{h}\right)}; h = 5.4 \text{ nm} \quad L = 231 \text{ nm}$$

Moles of hydroxyl groups on CNC. ²

$$N_0 = 8.13 \times 10^{-3} \text{ mmol/m}^2$$

$$A_{total} = \frac{m_{CNC}}{\rho_{cell}} \frac{2\pi H + 4(W - H)}{\pi W H}$$

$$\frac{A_{total}}{m_{CNC}} = \frac{1}{1.5 \frac{\text{g}}{\text{cm}^3}} \frac{2\pi(5.4 \text{ nm}) + 4(24.1 - 5.4)}{\pi(5.4 \text{ nm})(24.1 \text{ nm})} = 0.18 \times 10^3 \text{ m}^2/\text{g}$$

$$N_{OH} = 8.13 \times 10^{-3} \text{ mmol/m}^2 \times 0.18 \times 10^3 \text{ m}^2/\text{g}$$

$$N_{OH} = 1.4 \text{ mmol/g}$$

Crystallinity Index:

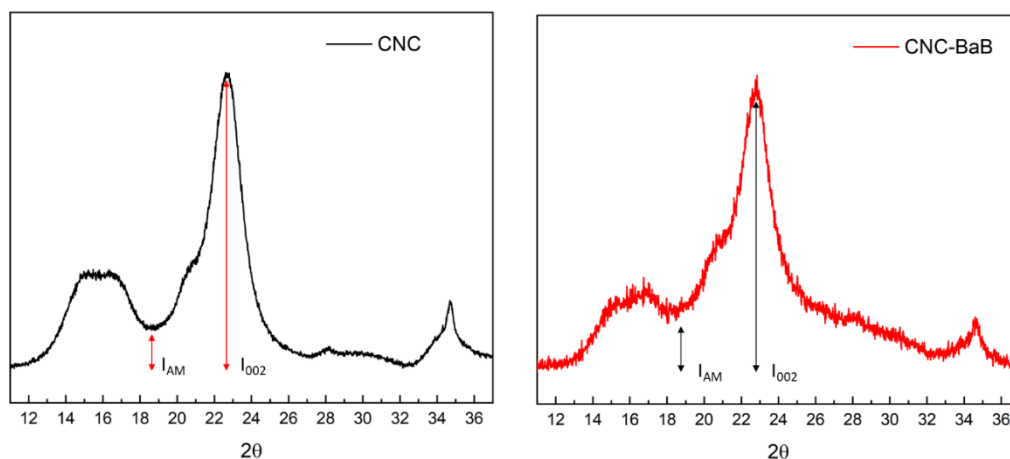


Figure S4: XRD profiles of unmodified (a) unmodified CNCs and (b) **CNC-Br**. Both particles exhibit peaks consistent with a cellulose I morphology.

Crystallinity index calculation for unmodified CNCs and **CNC-Br**.³

$$CI_{CNC} = \frac{(I_{002} - I_{AM})}{I_{002}} = \frac{(100 - 14.08)}{100} = 0.86$$

$$CI_{CNC-Br} = \frac{(I_{002} - I_{AM})}{I_{002}} = \frac{(100 - 16.93)}{100} = 0.83$$

CNC-Br Discoloration:

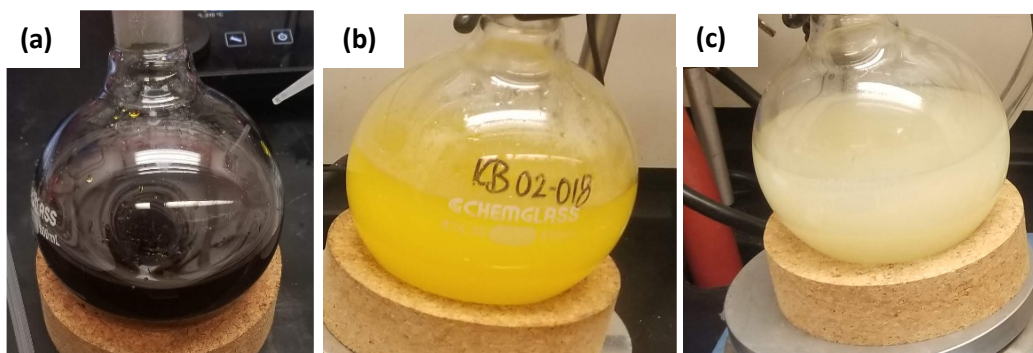


Figure S5: Reaction mixture of CNCs, BaB, and pyridine in DMF in which the CNCs underwent different drying scenarios. (a) Drying in vacuum over (60°C, 15 mbar), (b) drying overnight on high vacuum, (c) drying until 200 mmHg

1-4 Characterization:

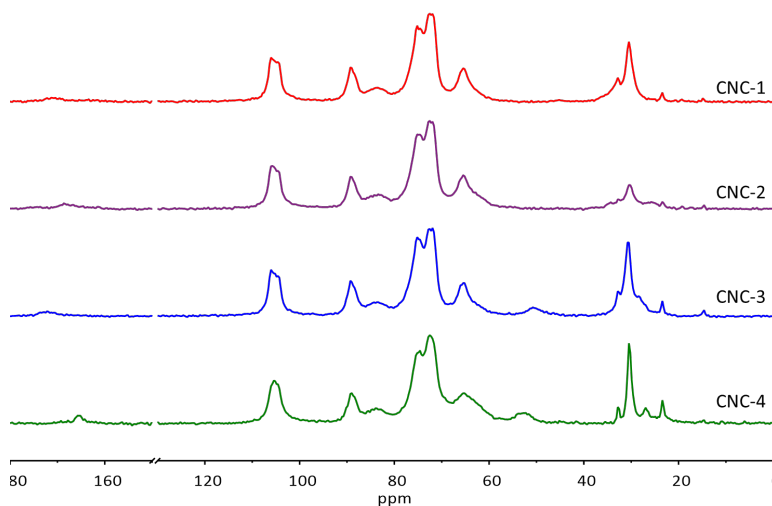


Figure S6: ^{13}C NMR of 12-carbon alkyl derivatives **CNC-1** – **CNC-4**. Alkane carbon peaks from 20-40 ppm support the successful attachment of the respective nucleophiles.

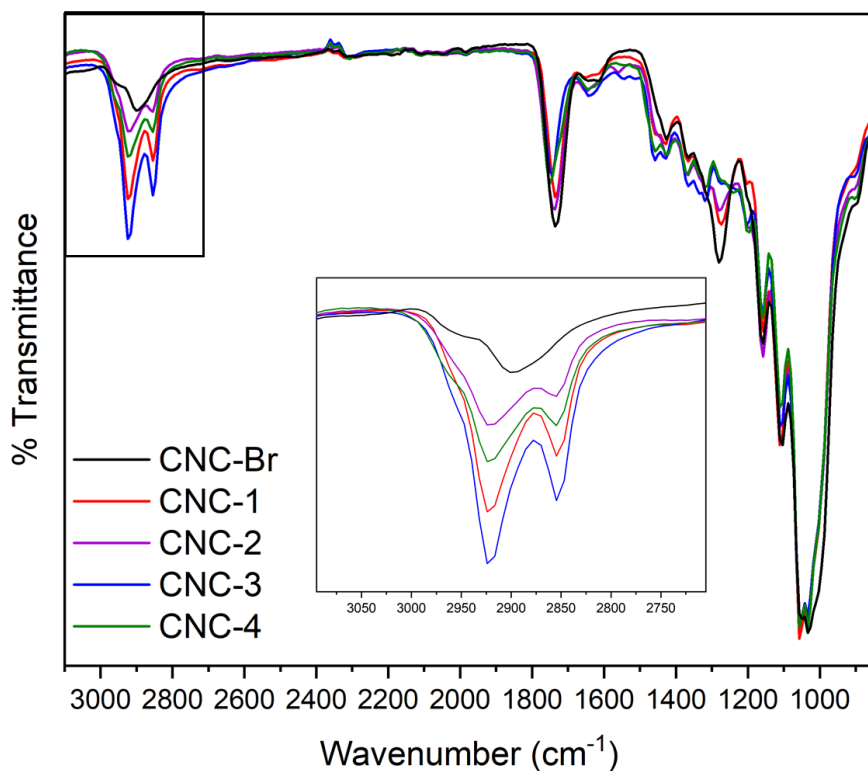


Figure S7: ATR-FTIR of **CNC-Br** and 12-carbon alkyl derivatives **CNC-1** – **CNC-4**. Inset represents the enlarged area for the C-H absorbance peak between 2700-3100 cm^{-1}

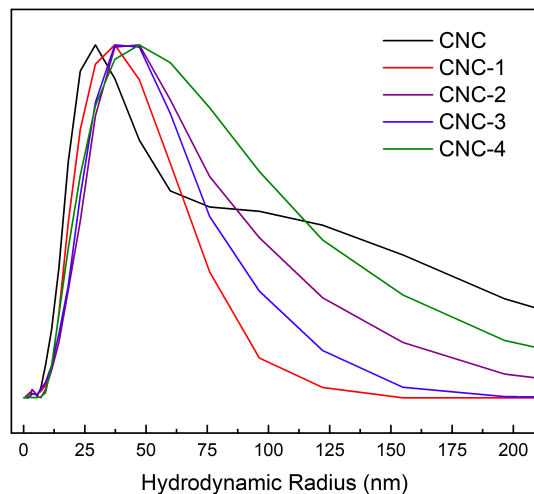


Figure S8: DLS particle size distribution of 12 carbon alkyl derivatives **CNC-1 – CNC-4** in a 3.8% H₂O in DMF solution.

Table S1: Hydrodynamic radius (R_h) for CNC derivatives

Sample	R_h (nm)
CNC	29.4
CNC-1	37.2
CNC-2	47.2
CNC-3	37.2
CNC-4	47.2

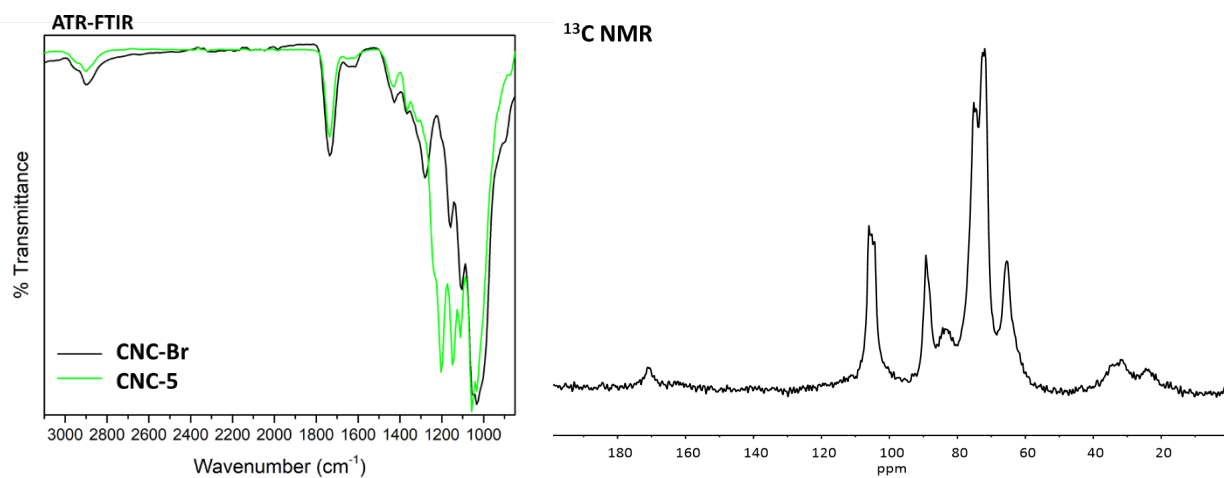


Figure S9: FTIR and ¹³C NMR spectra for **CNC-5**, modified with 1H,1H,2H,2H-Perfluorodecanethiol (**5**)

Elemental Analysis:

Based off the square-shape geometry in which the cellulose chains align in CNCs with a cellulose I crystal structure, the percent of surface chains can be calculated using the lattice plane d -spacing (0.61 and 0.51 nm) and the height ($h=5.4\text{nm}$) of the CNCs. Due to the 180° twist between the glucose units of each repeating cellulose unit, only half of the hydroxyl groups are accessible on the surface.⁴

$$OH_s\% = \frac{2\left(\frac{h}{0.54}\right) + 2\left(\frac{h}{0.61}\right)}{2(h \times h)(0.61 \times 0.51)} \times 100\% = \frac{\left(\frac{5.4}{0.54}\right) + \left(\frac{5.4}{0.61}\right)}{(5.4 \times 5.4)(0.61 \times 0.51)} \times 100\% = 21.3\%$$

To obtain the ratio of available surface hydroxyl groups to the total glucose units of the CNC, the number of hydroxyls in each glucose units (3) was multiplied by the percent of chains at the surface.

$$n(OH):n(Glu) = 3 \quad n(OH_s):n(Glu) = 3 * 0.213 = 0.64$$

Table S2: Elemental analysis data for unmodified CNCs.

	C	H	Br	S	N
%	42.47	6.19	0.00	0.78	0.00
mol/g	3.54	6.13	0.00	0.02	0.00

Calculating percent of sulfate groups in unmodified CNCs:

The carbon present in unmodified CNCs derives from the repeating glucose units, so the amount of glucose was calculated based on the carbon content. The sulfur derives solely from sulfates present on the surface. The sulfur amount was divided by the number of glucose units to get the ratio sulfated alcohols. This ratio was then divided by the theoretical amount of hydroxyl groups in the CNCs to obtain conversion in the bromoacetyl bromide reaction.

$$n(Glu) = \frac{n(C)}{6} = \frac{3.54}{6} = 0.59 \quad n(sulfate):n(Glu) = \frac{0.02}{0.59} = 0.04$$

$$\% OH \text{ conversion} = \frac{0.04}{0.64} \times 100\% = 6.5\%$$

Table S3: Elemental analysis data for CNC-Br

	C	H	Br	S	N
%	38.42	4.82	15.00	0.51	0.35
mol/g	3.20	4.77	0.19	0.02	0.02

Amount of Bromoester on surface of CNC-Br:

The carbon present in **CNC-Br** comes from both the bulk CNC and from the addition of **BaB**. For each bromine attached with **BaB**, there are 2 carbon atoms as well, thus allowing the deconvolution of the source of the carbons.

$$n(\text{Glu}) = \frac{n(\text{C}) - n(\text{C}_{\text{BaB}})}{6} = \frac{3.20 - 2(0.19)}{6} = 0.47$$

$$n(\text{Br}):n(\text{Glu}) = \frac{0.19}{0.47} = 0.40$$

To calculate the hydroxyl conversion, the amount of sulfate groups must be subtracted out from the available surface hydroxyl groups.

$$\% \text{ OH conversion} = \frac{n(\text{Br}):n(\text{Glu})}{n(\text{OH}_s):n(\text{Glu}) - n(\text{sulfate}):n(\text{Glu})} = \frac{0.40}{0.64 - 0.04} \times 100\% = 66.8\%$$

Table S4: Elemental analysis data for **CNC-1**

	C	H	Br	S	N
%	49.96	7.42	1.02	3.95	0.37
mol/g	4.16	7.35	0.01	0.12	0.03

Amount of dodecanethioether on surface of CNC-1:

With the addition of **1**, the carbon found from EA can come from cellulose, **BaB**, or the combination of **BaB** and **1**. There are 2 carbon atoms per bromine, and 14 carbon atoms per sulfur (after removing the sulfurs previously present from the sulfate groups) to account for the 12-carbon alkyl chain and the 2 from the **BaB** linker.

$$n(\text{Glu}) = \frac{n(\text{C}) - n(\text{C}_{\text{BaB}}) - n(\text{C}_{\text{thiol}} - \text{C}_{\text{sulfate}})}{6} = \frac{4.16 - 2(0.01) - 14(0.12 - 0.02)}{6} = 0.44$$

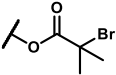
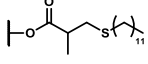
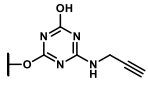
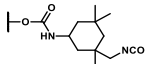
$$n(\text{S}):n(\text{Glu}) = \frac{0.11}{0.40} = 0.24$$

$$\% \text{ OH conversion} = \frac{n(\text{Br}):n(\text{Glu})}{n(\text{OH}_s):n(\text{Glu}) - n(\text{sulfate}):n(\text{Glu})} = \frac{0.24}{0.64 - 0.04} \times 100\% = 40.9$$

Table S5: Elemental analysis data for **CNC-3** and **CNC-4**

	%C	%H	%N
CNC-3	51.42	8.11	1.94
CNC-4	47.56	7.19	1.52

Table S6: Calculations for CNC modifications in the literature

Ref	Addition	C (%)	X (%)	n(C)/6	Modification/ Glucose	-OH Conversion	Notes
5		40.80	9.50 (Br)	$[C] - 4[Br]$	0.42	40.9	52 mL of BiB per 1 g of CNC
6		45.31	0.68 (S)	$[C] - (4 + 12)[S]$	0.04	6.2	
7		42.49	3.70 (N)	$[C] - \left(\frac{2}{3}\right)[N]$	0.13 0.18*	21 28*	*calculated 18 modifications per 100 glucose units
8		50.30	5.20 (N)	$[C] - 6[N]$	0.27	44.5	possibility of crosslinking

Characterization of CNC-6 – CNC-14:

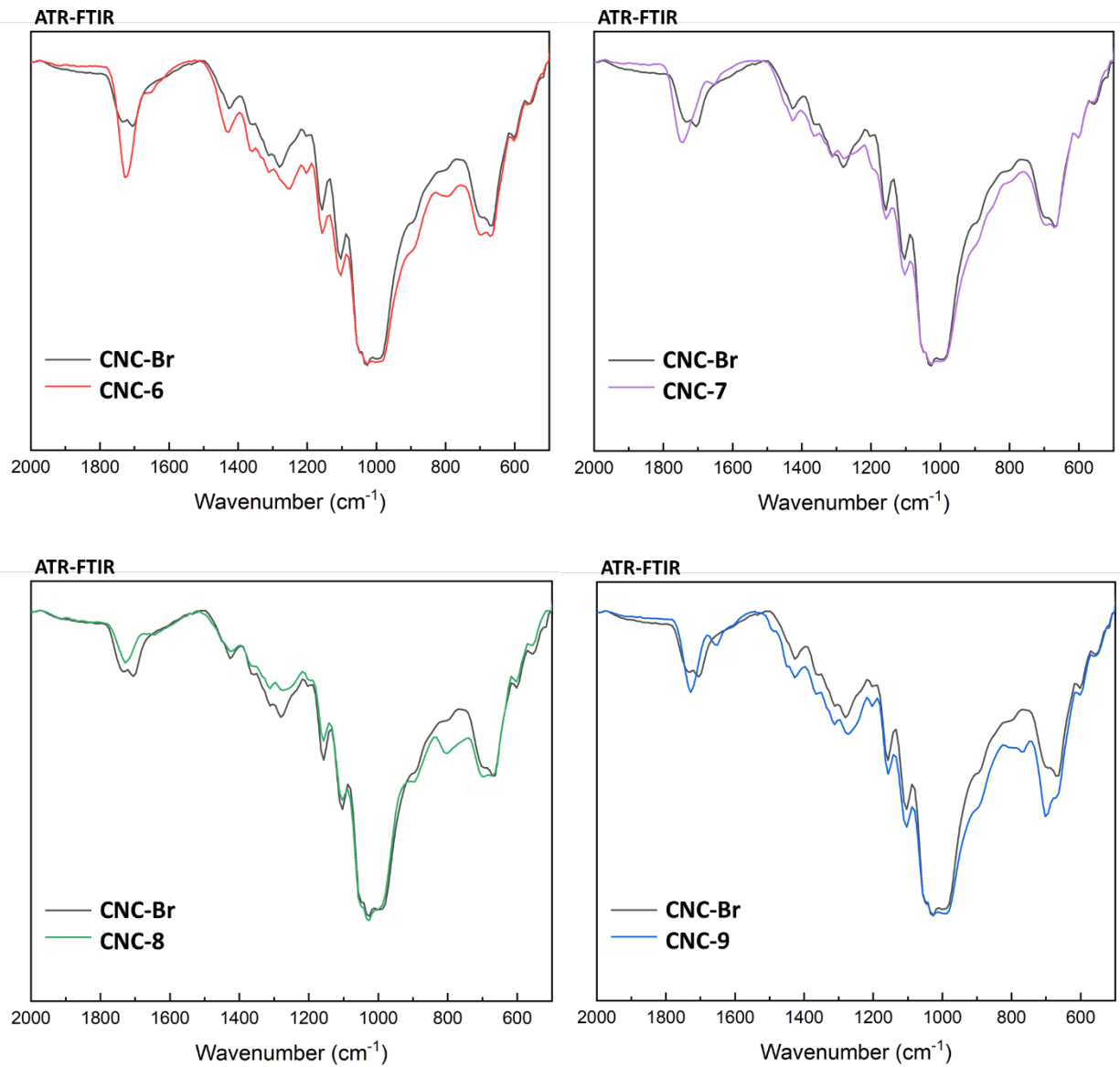


Figure S10: FTIR spectra for **CNC-6**, **CNC-7**, **CNC-8**, and **CNC-9** modified with methyl 3-mercaptopropionate (**6**), 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (**7**), (3-mercaptopropyl)trimethoxysilane (**8**), and benzyl mercaptan (**9**), respectively.

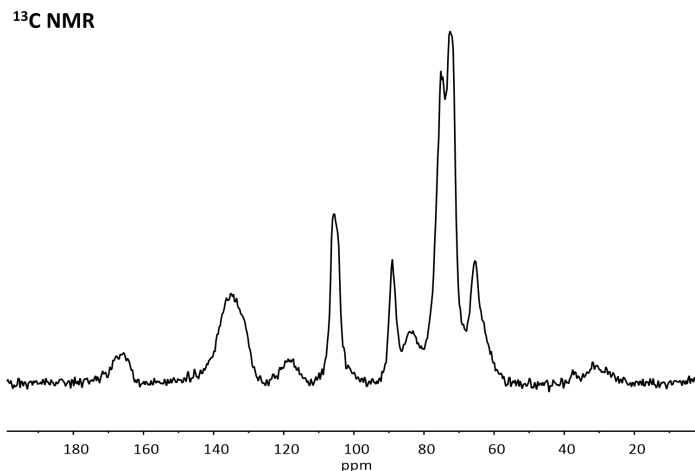


Figure S11: NMR spectrum for **CNC-10**, modified with triphenylphosphine (**10**)

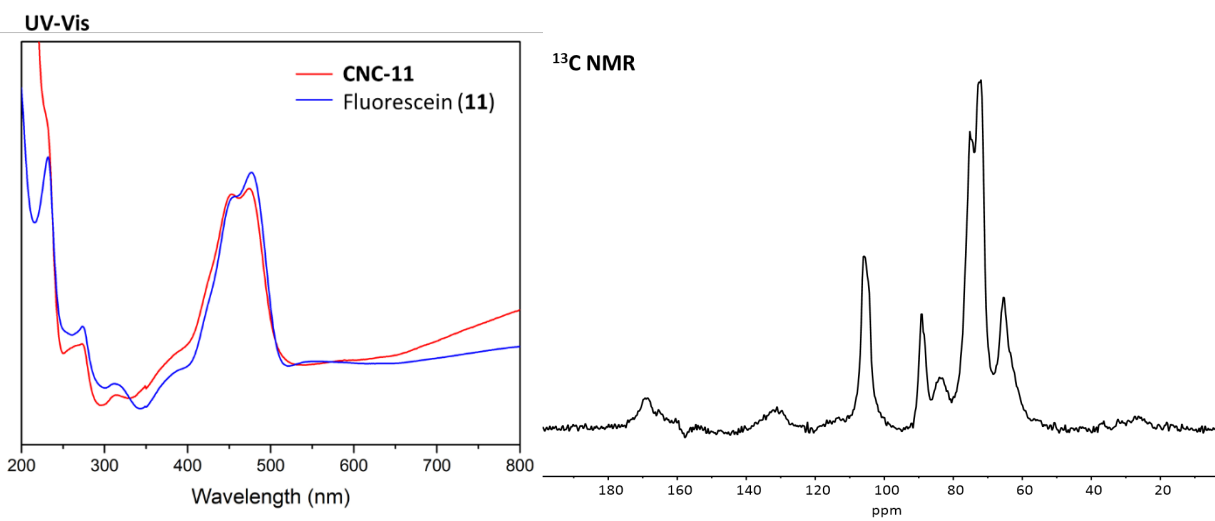


Figure S12: UV-Vis and NMR spectra for **CNC-11**, modified with fluorescein (**11**)

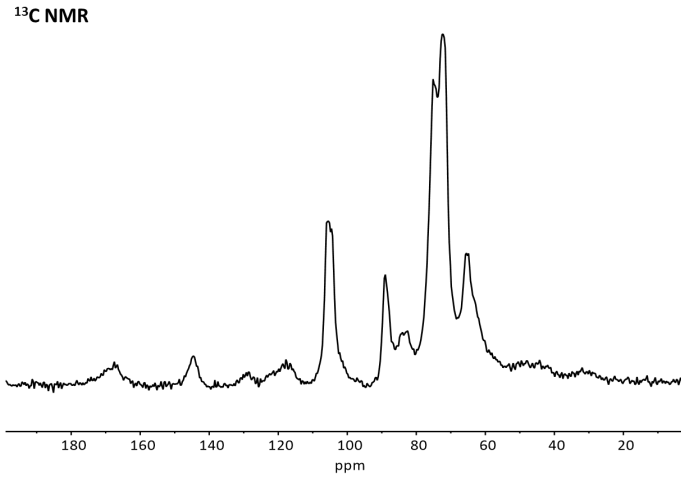


Figure S13: NMR spectrum for **CNC-12**, modified with dopamine (**12**)

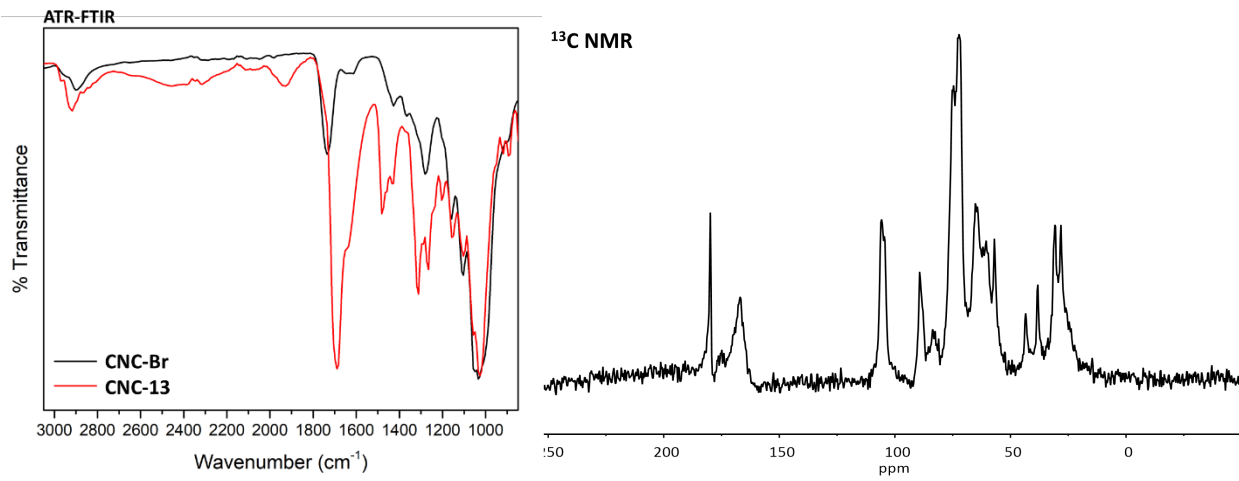


Figure S14: FTIR and ¹³C NMR spectra for **CNC-13**, modified with biotin (**13**)

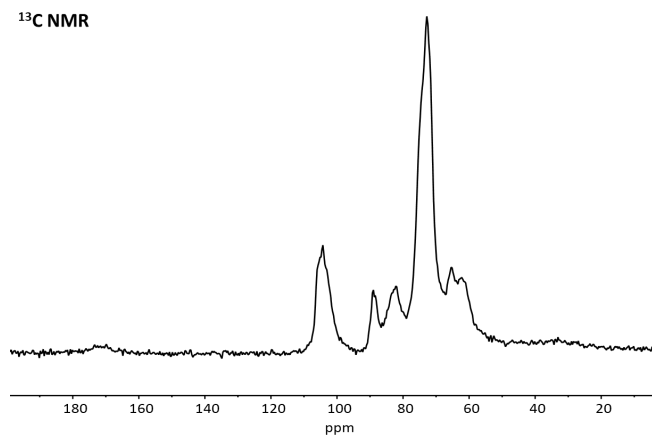
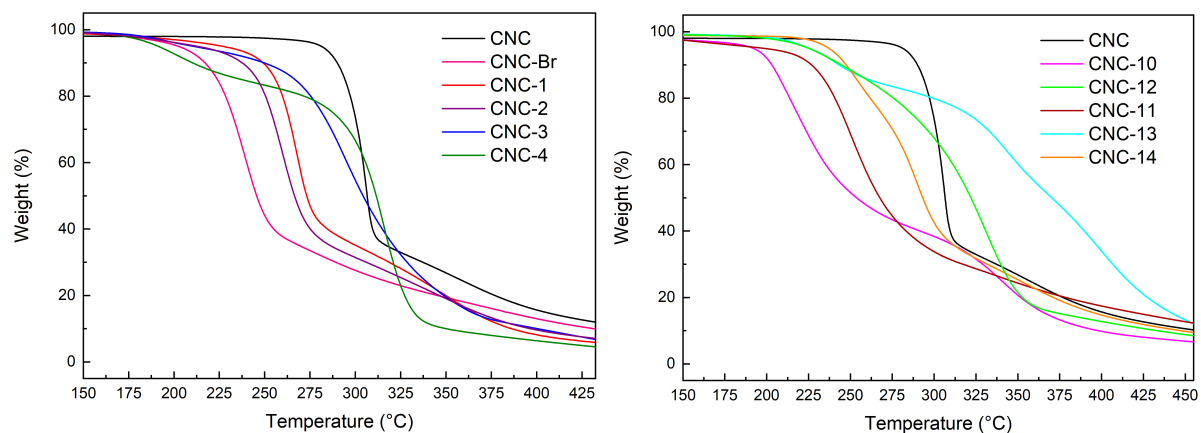


Figure S15: ¹³C NMR spectrum for **CNC-14**, modified with cyclodextrin monothiol (**14**)

Table S7: Elemental analysis data for **CNC-14**

	C	H	Br	S
%	37.71	5.54	0.81	1.74
mol/g	3.14	5.49	0.01	0.05

Thermal Stability:**Figure S16:** Thermogravimetric analysis for CNC, **CNC-Br**, **CNC-(1-4)**, and **CNC-(10-14)****Table S8:** Thermogravimetric analysis decomposition temperatures

Sample	T _{5%} (°C)	T _{50%} (°C)
CNC	284	307
CNC-Br	202	246
CNC-1	227	273
CNC-2	213	267
CNC-3	211	304
CNC-4	192	312
CNC-10	192	254
CNC-11	198	268
CNC-12	225	322
CNC-13	226	370
CNC-14	237	293

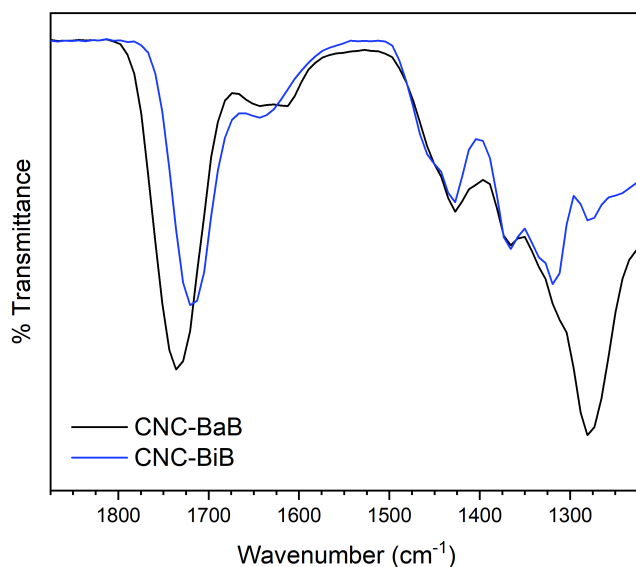


Figure S17: ATR-FTIR of CNC-Br and CNC-BiB

Table S9: Elemental analysis data for CNC-BiB

	C	H	Br
%	40.31	6.35	8.52
mol/g	3.36	6.29	0.11

Amount of BiB on surface of CNC-BiB:

Each bromine atom has 4 carbons atoms with the addition of **BiB** on the CNC.

$$n(\text{Glu}) = \frac{n(\text{C}) - n(\text{C}_{\text{BiB}})}{6} = \frac{3.36 - 4(0.11)}{6} = 0.49$$

$$n(\text{Br}):n(\text{Glu}) = \frac{0.11}{0.49} = 0.22$$

$$\% \text{ OH conversion} = \frac{n(\text{Br}):n(\text{Glu})}{n(\text{OH}_s):n(\text{Glu}) - n(\text{sulfate}):n(\text{Glu})} = \frac{0.22}{0.64 - 0.04} \times 100\% = 36.5\%$$

References:

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