

Supporting Information

Synthesis and characterization of halloysite-cyclodextrin nanosponges for enhanced dyes adsorption

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Experimental Details

Methylene blue, toluidine blue, methyl orange and congo rubin were purchased from Merck company, bromocresol green and rhodamine B were purchased from Carlo Erba; all dyes were used without further purification. Thiol-functionalized HNTs and heptakis-6-(tert-butyldimethylsilyl) 2-allyloxy- β -cyclodextrin (β CDs) were prepared according to previous reports.¹

Halloysite used in this study is the Matauri Bay halloysite from Northland, New Zealand, supplied by Imerys Tableware, New Zealand.

Microwave-assisted syntheses were carried out with a CEM DISCOVER monomode system in a closed vessel.

Thermogravimetric analyses were performed on a Q5000 IR apparatus (TA Instruments) under a nitrogen flow of 25 cm³ min⁻¹ for the sample and 10 cm³ min⁻¹ for the balance. The weight of each sample was ca. 10 mg. Measurements were carried out by heating the sample from room temperature up to 900 °C at a rate of 10 °C min⁻¹.

IR spectra (KBr) were recorded with an Agilent Technologies Cary 630 FT-IR spectrometer. Specimens for these measurements were prepared by mixing 5 mg of the sample powder with 100 mg of KBr.

ζ -potential and dynamic light scattering (DLS) measurements were taken by using microelectrophoretic ZetaPlus Potential Analyzer (Brookhaven Instruments) at 25.0 \pm 0.1 C.

Halloysite-cyclodextrin nanosponges were imaged by Scanning Electron Microscope 22 (Hitachi S4800 FE-SEM). The halloysite samples were coated with 1 nm gold by Cressington 23 Sputter Coater (208HR) before the imaging;

For TEM observation the samples were prepared using a drop of suspension solution (p-HNTs and HNT-CDs) on formvar-coated copper grid (400 mesh) and allowing the drop to dry completely in a vacuum desiccator. The TEM images of the samples were obtained using a Philips TEM CM 100 transmission electron microscope at accelerating voltage = 80 kV.

The dispersion were agitated in an orbital shaker (VWR) at a constant speed of 250 rpm.

The specific surface area and pore site distribution was made by N₂ adsorption/desorption Nova 2200 Quantachrome Instruments analyzer.

UV-vis measurements were performed using a Beckmann DU 650 spectrometer.

Synthesis of heptakis-6-(tert-butyldimethylsilyl)-2-allyloxy- β -cyclodextrin.

In a 500 mL round bottom flask NaH powder (60%, 0.790 g, 32 mmol) was weighed and under constant stirring, at 0 °C and Ar atmosphere were added 120 mL of DMF. After 10 minutes a solution of of heptakis-6-(tert-butyldimethylsilyl)- β -cyclodextrin (5 g, 26 mmol) in

DMF (25 mL) was added dropwise. The reaction was allowed to stir at 0 °C for 30 min and then overnight at room temperature. The reaction vessel was cooled to 0 °C, and allyl bromide (1.64 mL, 18.95 mmol) was added dropwise. The reaction was then allowed to stir overnight at room temperature. The reaction was evaporated to dryness, and the residue was dissolved in CH₂Cl₂ (250 mL) and washed with water (3x150 mL) and finally with brine (150 mL). The organic layer was dried (MgSO₄), filtered, and evaporated to dryness to afford a white foam. Purification by column chromatography (SiO₂, hexane/AcEt 8:1, 6:1 and 4:1) afforded a yellow foam with a yield of 25%.

¹H-NMR (CDCl₃, 300 MHz) δ: 0.04 (s, 21H, Si(CH₃)), 0.05 (s, 21H, Si(CH₃)), 0.89 (s, 63H, C(CH₃)₃), 3.31-3.35 (dd, 7H, H(2)); 3.51-3.68 (m, 21H, H(4), H(5), H(6a)); 3.92-4.00 (m, 14H, H(6b), H(3)); 4.21-4.27 (m, 7H, OCH_A); 4.47-4.53 (dd, 7H, OCH_B); 4.92 (d, 7H, H(1)); 5.21-5.35 (m, 14H, CH=CH₂); 5.90-6.03 (m, 7H, CH=CH₂).

¹³C-NMR (CDCl₃, 300 MHz) δ: 5.2 (SiCH₃), -5.1 (SiCH₃), 18.3 (C(CH₃)₃), 25.9 (C(CH₃)₃), 61.7 (C-6), 71.6, 79.5, 82.0 (C-2, C-3, C-4, C-5), 73.2 (OCH₂), 101.1 (C-1), 118.2 (CH₂=CH), 134.3 (CH₂=CH).

Synthesis of CDs polymer.

Heptakis-6-(tert-butyldimethylsilyl) 2-allyloxy-β-cyclodextrin (200 mg) was weighed in a MW test tube provided with a cap and a catalytic amount of AIBN was added. The mixture was inserted in the MW apparatus at 100 °C, under constant stirring, for 1 h. Successively, the solid was filtered off, rinsed several times with CH₂Cl₂ (until the unreacted reagents were not detected by TLC) and dried at 80 °C under vacuum.

¹H-NMR (DMSO, 300 MHz) δ: 0.04 (s, Si(CH₃)), 0.05 (s, Si(CH₃)), 0.89 (s, C(CH₃)₃), 3.31-3.35 (m); 3.51-3.68 (m); 3.92-4.00 (m); 4.21-4.27 (m); 4.47-4.53 (m); 4.92 (m); 5.21-5.35 (m); 5.90-6.03 (m).

¹H-NMR of the CD polymer compared to the one of β-CDs shows broad signals, typical of not symmetric cyclodextrin modifications.

Synthesis of HNT-SH scaffold

First, 1 g of HNT was weighted in a MW test tube provided with a cap, and 2 mL of 3-mercaptopropyl trimethoxysilane was added dropwise. The mixture was dispersed ultrasonically for 5 min at room temperature and inserted in MW apparatus at 100 °C, under constant stirring for 1h. The powder was filtered, rinsed with MeOH and dried at 80 °C overnight.

Synthesis of HNT-CDs nanosponge hybrids

Thiol-functionalized HNTs (200 mg) and heptakis-6-(tert-butyldimethylsilyl) 2-allyloxy- β -cyclodextrin (200 or 300 mg) were weighed in a MW test tube provided with a cap and a catalytic amount of AIBN was added. The mixture was inserted in the MW apparatus at 100 °C, under constant stirring, for 1 h. Successively, the solid was filtered off, rinsed several times with CH₂Cl₂ and CH₃OH (until the unreacted reagents were not detected by TLC) and dried at 80 °C under vacuum.

Swelling properties

Water sorption capacity of HNT-CDs nanosponge hybrid was determined gravimetrically. The nanomaterial with determined weight was immersed for 1 h in distilled water at room temperature until swelling equilibrium was reached. After this time water was removed and the nanomaterial weighted using analytical balance. Water excess was removed using filter paper prior weighting. The swelling ratio (SR) was calculated using the equation:

$$SR (\%) = \frac{(W_s - W_d)}{W_d} \cdot 100 \quad (\text{Eq. S.1})$$

where W_s and W_d are the weights of the hybrid at the swelled and the dry state, respectively. Experimental data were expressed as the mean \pm standard deviation (SD) for $n=3$.

Batch adsorption experiments

All adsorption experiments were conducted on sealed vessels containing 5.0 mg of HNT-CDs hybrid and 2 mL of RB solution (2×10^{-5} M) in HCl 0.1 N, acetate buffer pH 4.24 and phosphate buffer pH 7.4 at 277, 298, 310 and 331 K, respectively. The obtained dispersion were vigorously vortexed and shaken in a thermostatic shaker with a shaking of 200 rpm at 25 °C. The supernatant were obtained by centrifugation for detecting RB concentration via UV-vis spectrophotometer at the maximum absorption wavelength of 550 nm. The removal efficiency (RE (%)) was calculated by:

$$RE (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (\text{Eq. S.2})$$

where C_0 and C_e are initial and equilibrium concentrations of RB (M), respectively.

Adsorption isotherms

The adsorption isotherms of HNT-CDs hybrids were obtained by weighing 5 mg of HNT-CDs nanosponge in the presence of RB solution in a concentration range of 5×10^{-6} - 7.5×10^{-5} M,

in HCl 0.1 N, acetate (0.01 M) buffer pH 4.54 and phosphate buffer pH 7.4, and shaken in a thermostated shaker with a shaking of 200 rpm for 12 h to reach equilibrium at 298 K. The equilibrium adsorption capacity Q_e (mol g⁻¹) was calculated by the following equation:

$$Q_e = \frac{(C_0 - C_e) \cdot V}{M} \quad (\text{Eq. S.3})$$

where C_0 and C_e are initial and equilibrium concentrations of RB (M), respectively, M is the weight of HNTs (g) and V is the volume of RB solution (L).

Adsorption kinetics

The batch experiments were carried out for investigating the adsorption kinetics of RB onto HNT-CDs nanosponge hybrid at room temperature in acetate buffer (0.01 M) pH 4.54. For all experiments, HNT-CDs nanosponge hybrid (5 mg) were added into 2 mL solution of RB (2.5×10^{-5} M). The amount of RB adsorbed at time t (Q_t , mol g⁻¹) was calculated by the following equation:

$$Q_t = \frac{(C_0 - C_t) \cdot V}{M} \quad (\text{Eq. S.4})$$

where C_0 and C_t are initial and t time concentrations of RB (M), respectively, M is the weight of HNTs (g) and V is the volume of RB solution (L).

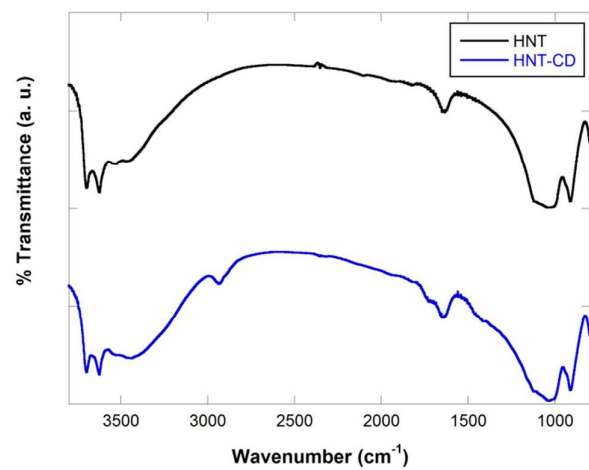


Figure S1. FTIR spectra of HNT and HNT-CD nanosponge hybrid.

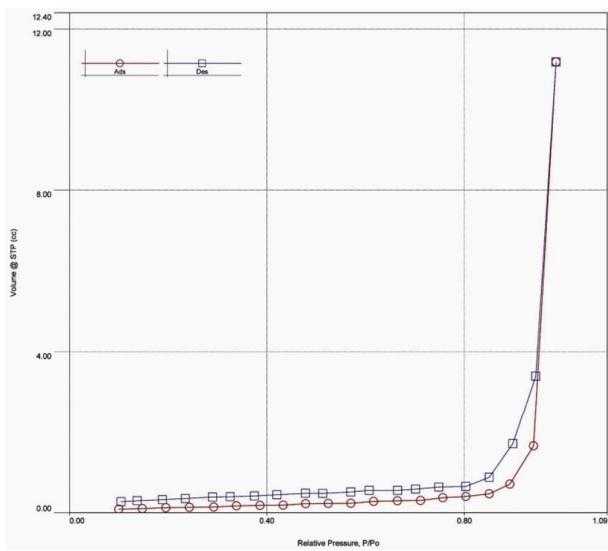


Figure S2. N₂ adsorption-desorption isotherm of HNT-CD nanosponge hybrid.

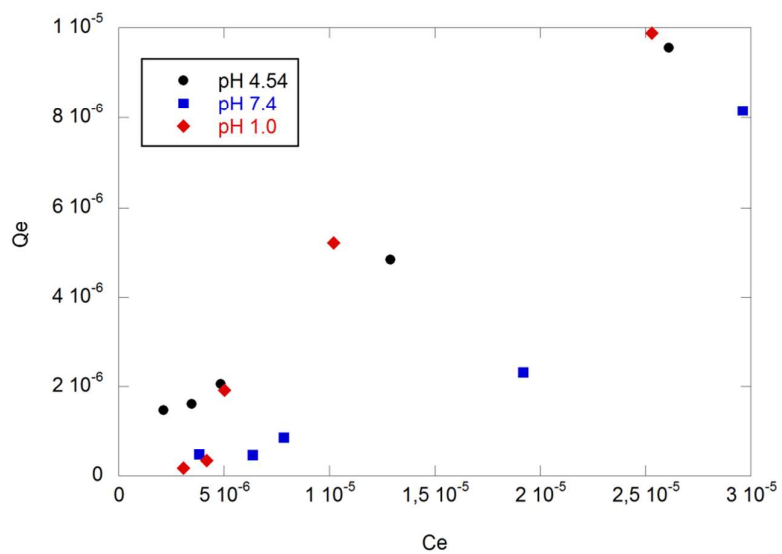


Figure S3. Adsorption isotherms of RB on HNT-CD (40%) nanosponge hybrid in HCl 0.1 N, acetate buffer pH 4.54 and phosphate buffer pH 7.4.

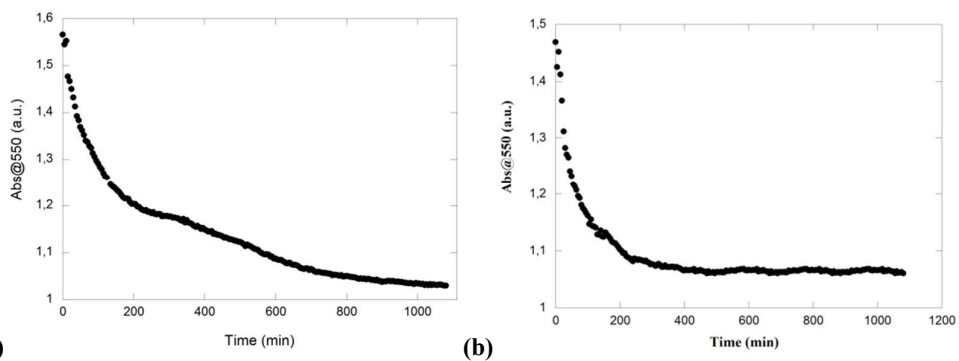


Figure S.5. Kinetic adsorption of RB on HNT-CD (a) (20%); (b) (40%) in acetate buffer pH 4.54.

Table S.1. Adsorption kinetic parameters of RB onto HNT-CD nanospheres hybrids.

	<i>First-order</i>			<i>Second-order</i>			<i>Weber-Morris</i>	
	$Q_t = Q_e \cdot (1 - e^{-k_1 t})$			$Q_t = Q_e \cdot \left(\frac{Q_e k_2 t}{1 + Q_e k_2 t} \right)$			$Q_t = kt^{1/2} + C$	
	Q_e	k_1	R^2	Q_e	k_2	R^2	k_{IPD}	R^2
1	$(5.27 \pm 0.01) \times 10^{-6}$	0.024 ± 0.001	0.565	$(5.51 \pm 0.02) \times 10^{-6}$	$(8.32 \pm 0.03) \times 10^4$	0.903	$(2.59 \pm 0.08) \times 10^{-9}$	0.874
2	$(5.27 \pm 0.01) \times 10^{-6}$	0.100 ± 0.006	0.399	$(5.37 \pm 0.01) \times 10^{-6}$	$(3.5 \pm 0.1) \times 10^5$	0.844	$(2.6 \pm 0.2) \times 10^{-8}$	0.556

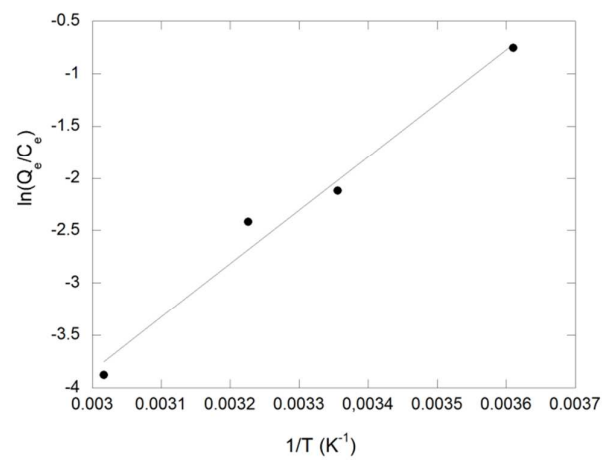


Figure S.6. Temperature dependent adsorption of RB on HNT-CDs nansoponge hybrid.

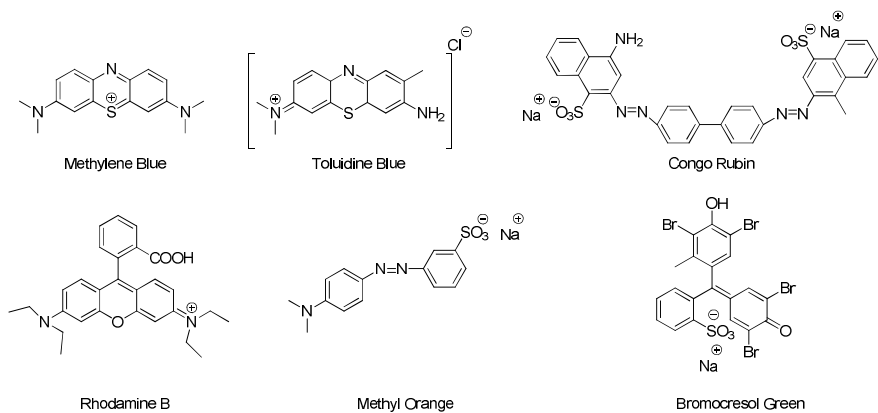


Figure S.7. Structure of the investigated anionic and cationic dyes.

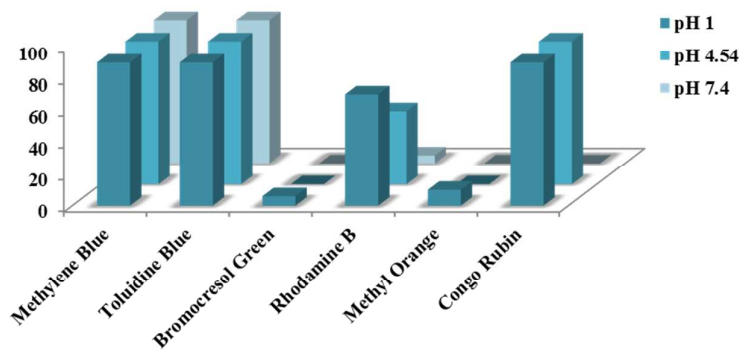


Figure S.8. Adsorption capacities of p-HNT for the different dyes at pH 1.0, 4.54 and 7.4.

Table S.2. Comparison between the adsorption performances of pristine HNT and HNT-CD (40%) hybrid.

Organic Dye	HNT-CD (40%)			HNT		
	pH 1	pH 4.54	pH 7.4	pH 1	pH 4.54	pH 7.4
Methylene Blue	100	100	100	90	90	90
Toluidine Blue	100	100	100	90	90	90
Bromocresol Green	8	9	0	6	0	0
Rhodamine B	80	71	24	70	46	5
Methyl Orange	16	13	4	10	0	0
Congo Rubin	100	100	39	90	90	0

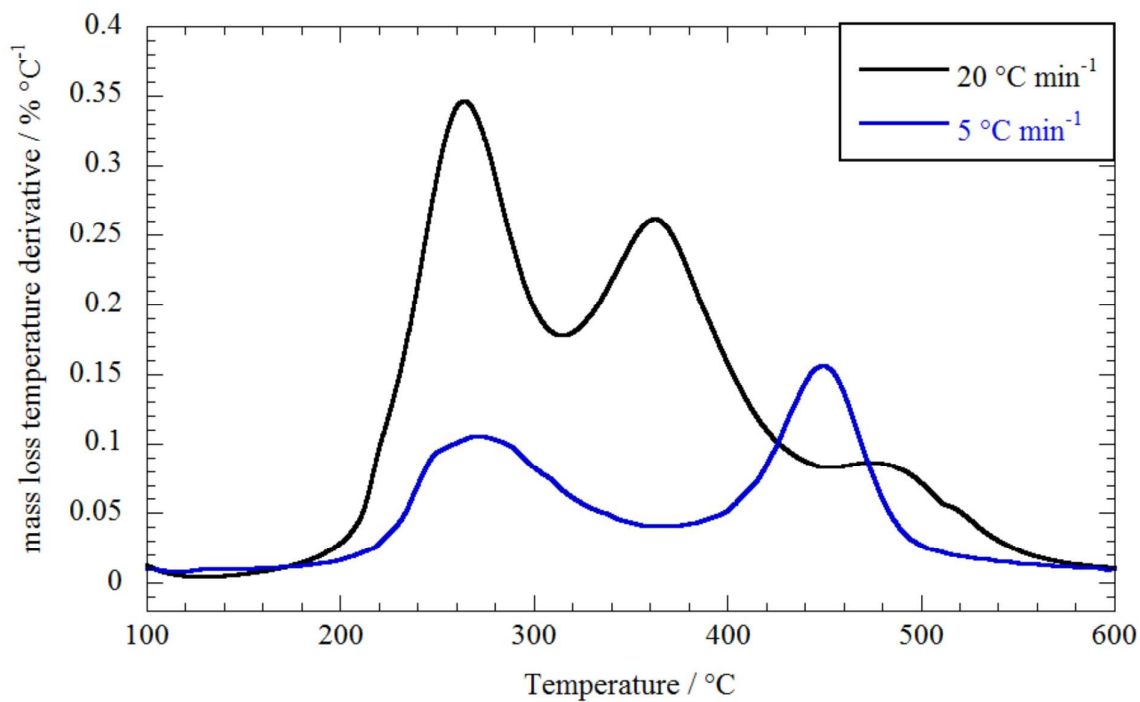


Figure S.9. Differential thermal analysis curves for HNT-CD hybrid 40% at two heating rates.

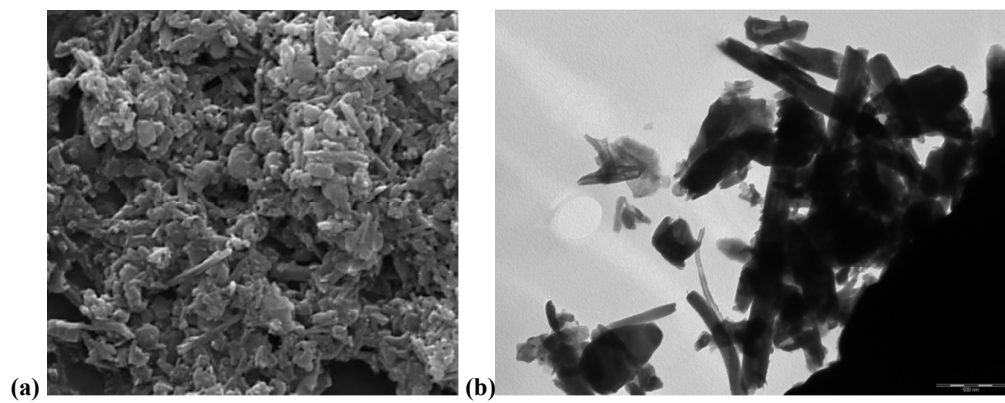


Figure S10. (a) SEM and (b) TEM images of HNT-CD (20%).

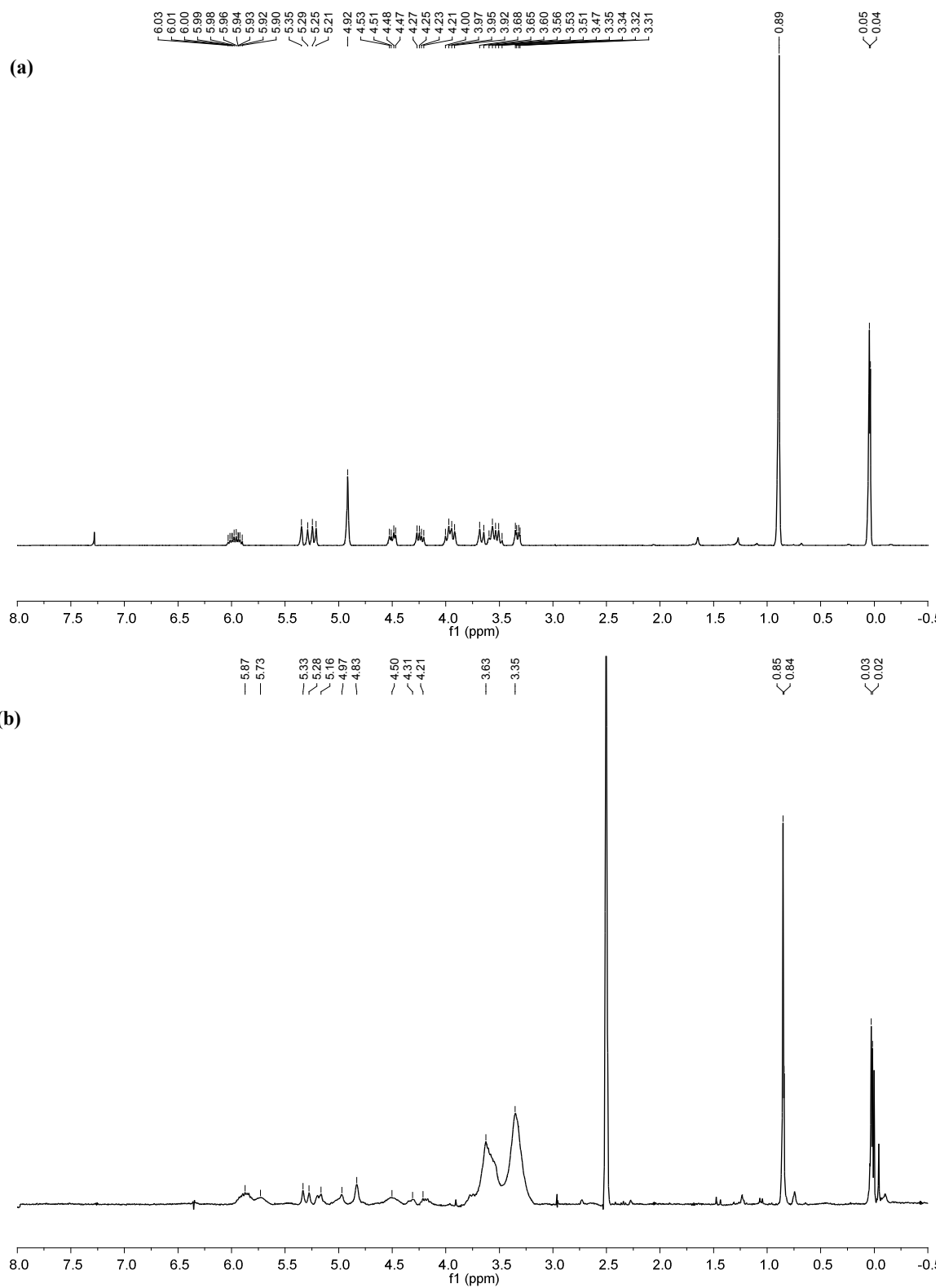


Figure S11. $^1\text{H-NMR}$ spectra of (a) β -CDs and (b) CD cross-linked polymer.

REFERENCES:

1. M. Massaro, S. Riela, P. Lo Meo, R. Noto, G. Cavallaro, S. Milioto and G. Lazzara, *J. Mater. Chem. B*, 2014, 2, 7732-7738.