Supplementary Information

## Stimuli-responsive nanoparticles from ionic cellulose derivatives

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## FTIR spectroscopy

FTIR spectroscopy was conducted on Spectrum One FTIR Spectrometer (PerkinElmer, Massachusetts, USA) using the ATR technique at RT between 4000 and 600 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. The samples were measured twice per 32 scans and an average spectrum was then generated for each sample. Baseline correction was conducted using the method 'concave rubber band algorithm' with 200 baseline points and 5 iterations.



**Fig. S1.** FTIR spectra of (a) microcrystalline cellulose (MCC), (b) CUE, (c) CUE-MPA, CUE-CA, (e) CUE-DMAET and (f) CUE-DEAET.

Comparing the FTIR spectrum of MCC and CUE (Fig. S1a and S1b), the peak at 3325 cm<sup>-1</sup> ascribed to stretching vibrations of hydroxyl groups at cellulose backbone totally disappeared

after the esterification. Within the FTIR spectrum of CUE, new bands emerge at 3077, 1740, 1640 and 993/907 cm<sup>-1</sup>, which are attributed to stretching vibrations of CH<sub>2</sub>=CH<sub>2</sub>, stretching vibrations of C=O, stretching vibrations of C=C, and deformation vibrations of alkene C-H groups, respectively.<sup>[1]</sup> The intensities of signals at 2928 and 2856 cm<sup>-1</sup> strongly increased, which are due to asymmetric and symmetric stretching vibrations of C-H groups of alkyl chains, respectively.<sup>[1a]</sup>

Within the FTIR spectra of CUE-MPA, CUE-CA, CUE-DEAET and CUE-DMAET, the bands related to vinyl groups at 3077, 1640, 993 and 907 cm<sup>-1</sup> disappeared, while new signals are visible. CUE-MPA displays a distinct signal at 1706 cm<sup>-1</sup> which is attributed to stretching vibrations of carboxyl groups. CUE-CA demonstrates a new band at 1595 cm<sup>-1</sup> which is derived from deformation vibrations of N-H groups, indicating the introduction of (2-aminoethyl)thiol groups. CUE-DEAET and CUE-DMAET display a broad absorption signal at 2250-2700 cm<sup>-1</sup> which is attributed to stretching vibrations of N-H groups of amine hydrohalide, confirming the introduction of 2-(diethylamino)ethanethiol groups or 2-(dimethylamino)ethanethiol groups. In addition, the signals at 3410 and 1635 cm<sup>-1</sup> ascribed to O-H vibrations are derived from moisture.



**Fig. S2.** (a) <sup>13</sup>C and (b) <sup>1</sup>H NMR spectrum of CUE in CDCl<sub>3</sub>. The inset in (a) shows the representative chemical structure of CUE with numbered carbons.

<sup>13</sup>C NMR spectrum of CUE shows the signals ascribed to cellulose backbone and 10-undecenoyl groups. The signals at 172.8, 172.3, and 171.7 ppm are attributed to the carbons in C=O groups at the C-6, C-3, and C-2 position of AGUs, respectively.<sup>[2]</sup> The signals at 114 and 139 ppm are derived from carbons in terminal olefin groups, while the weak signals between 60 and 105 ppm are due to the carbons at cellulose backbone. Moreover, signals between 40 and 10 ppm are attributed to the saturated aliphatic chains of 10-undecenoyl moieties. Within the <sup>1</sup>H NMR spectrum of CUE, the signals around 4.8 and 5.7 ppm are ascribed to protons of terminal olefin protons of 10-undecenoyl groups. The signals in the region of 3.2 to 5 ppm are due to the protons at cellulose backbone except for the signal at 4.8 ppm. The signals between 1.2 and 2.3 ppm are derived from the protons in saturated aliphatic chains of 10-undecenoyl moieties.<sup>[1b, 1c]</sup>

## DS of CUE

The degree of substitution (DS) ascribed to 10-undecenoyl groups of CUE was calculated using the integrals of proton signals within <sup>1</sup>H NMR spectrum of CUE according to the following equation:

$$\frac{DS}{7} = \frac{I_{CH}}{I_T - 2I_{CH}}$$

where  $I_{CH}$  = the integration of the signal at 5.80 ppm ascribed to the proton of C16;  $I_{T}$ -2 $I_{CH}$  = the integration of protons ascribed to cellulose backbone.

Based on <sup>1</sup>H NMR spectrum in Fig. S3, the DS of CUE was calculated to be 3.



**Fig. S3.** A representative <sup>1</sup>H NMR spectrum of CUE in CDCl<sub>3</sub> for the calculation of the degree of substitution.



**Fig. S4.** (a) <sup>13</sup>C and (b) <sup>1</sup>H NMR spectrum of CUE-MPA. \* Butylated hydroxytoluene (BHT) residue as stabilizer in THF. The inset in (a) shows the representative chemical structure of CUE-MPA with numbered carbons.



Fig. S5. 2D NMR spectra of CUE-MPA: (a) <sup>1</sup>H, <sup>1</sup>H-COSY and (b) <sup>1</sup>H, <sup>13</sup>C-HSQC measurement.

Within the <sup>13</sup>C NMR spectrum of CUE-MPA (Fig. S4 and S5), the signals at 26.8 and 34.4 ppm are derived from carbons in  $CH_2$  next to carboxyl group (C-b<sub>1</sub>) and carbons in  $CH_2$  next to thioether bonds (C-a<sub>1</sub>), respectively. Within the <sup>1</sup>H NMR spectrum of CUE-MPA, new signals appear at 2.4 and 2.6 ppm, which are ascribed to protons in  $CH_2$  next to thioether bonds and  $CH_2$  next to carboxyl groups, respectively.



**Fig. S6.** (a) <sup>13</sup>C and (b) <sup>1</sup>H NMR spectrum of CUE-CA. \* Impurity from methanol. The inset in (a) shows the representative chemical structure of CUE-CA with numbered carbons.



Fig. S7. 2D NMR spectra of CUE-CA: (a) <sup>1</sup>H, <sup>1</sup>H-COSY and (b) <sup>1</sup>H, <sup>13</sup>C-HSQC measurements.

Within the <sup>13</sup>C NMR spectrum of CUE-CA (Fig. S6 and S7), the signals at 28.3 and 38.6 ppm are assigned to the carbons of the  $CH_2$  of (2-aminoethyl)thiol groups. The signals due to correlated protons are visible at 2.9 and 3.2 ppm within the <sup>1</sup>H NMR spectrum of CUE-CA.



**Fig. S8.** (a) <sup>13</sup>C and (b) <sup>1</sup>H NMR spectrum of CUE-DEAET. The inset in (a) shows the representative chemical structure of CUE-DEAET with numbered carbons.



**Figure S9.** (a) <sup>13</sup>C and (b) <sup>1</sup>H NMR spectrum of CUE-DMAET. The inset in (a) shows the representative chemical structure of CUE-DMAET with numbered carbons.

Fig. S8 and S9 show the <sup>13</sup>C and <sup>1</sup>H NMR spectra of CUE-DEAET and CUE-DMAET, respectively. The complete disappearance of CUE terminal olefin signals at 114 and 139 ppm in <sup>13</sup>C NMR spectra as well as at 4.8 and 5.7 ppm in <sup>1</sup>H NMR spectra confirm the modification of the terminal vinyl groups by 2-(diethylamino)ethanethiol hydrochloride or 2-(dimethylamino)ethanethiol hydrochloride. Furthermore, all expected structural features from both ionic cellulose derivatives were found in the <sup>13</sup>C and <sup>1</sup>H NMR spectra, such as 9.4 ppm (Cd<sub>3</sub>, -CH<sub>3</sub>), 52.9 ppm (C-b<sub>3</sub>, -CH<sub>2</sub>), 3.0 ppm (H-a<sub>3</sub>, -CH<sub>2</sub>) in the case of CUE-DEAET, and 43.7 ppm (C-c<sub>4</sub>, -CH<sub>3</sub>), 58.1 ppm (C-b<sub>4</sub>, -CH<sub>2</sub>), 3.0 ppm (H-a<sub>4</sub>, -CH<sub>2</sub> and H-c<sub>4</sub>, -CH<sub>3</sub>) in the case of CUE-DMAET.



**Fig. S10.** (a) Photo images of dispersions after dropping CUE-CA solutions (4 mg/ml) into water and further increase of pH values with aqueous NaOH solutions; (b) DLS measurement of obtained dispersions.

As shown in Fig. S10, CUE-CA could not form stable NPs in water. For the pH values from 4.5 to 8, NPs suspensions are transparent and contain multi-modally distributed aggregates as shown by DLS measurements. When the pH increased to 9, obvious aggregation can be observed.



**Fig. S11.** Photo images of dispersions after dropping CUE-DEAET (a) and CUE-DMAET (b) solutions into water and further increase of pH values with aqueous NaOH solutions.

The suspensions of CUE-DEAET and CUE-DMAET in water were transparent at the pH values 4.2 (or 4.5) and 5.0. When the pH increased to 6, opalescent suspensions formed. When the pH increased to 9, the transparency decreased significantly for the suspensions of both polymers, indicating a severe aggregation.



**Fig. S12.** (a) Photo images of NPs dispersions of CUE-MPA after adjusting the pH value from pH 7 to pH 3 and from pH 7 to pH 10; (b) Z-average diameters and PDI of obtained NPs.

As show in Fig. S12, the size of NPs from CUE-MPA stayed stable between the pH values of 4.5-10. At pH 3, severe aggregation can be observed.



Fig. S13. Representative SEM images of dried NPs of CUE-DEAET formed at pH 4.

Technique	CUE-MPA solutions		Water	Z-average		Zeta	
	Concentration (mg/ml)	Volume (ml)	(ml)	(nm)	PDI	(mV)	
dropping	2	1	10	85±1	0.131	-49.4±1.2	
	4	1	10	139±1	0.148	-47.1±0.5	
	6	1	10		0.490	-56.4±0.6	
dialysis	2	5	500	150±2	0.078	-43.6±0.1	
	4	5	500	200±2	0.131	-48.1±1.4	
	6	5	500	321±6	0.151	-45.3±0.5	

 Table S1. Characters of obtained NPs from CUE-MPA

	Polymer solutions		Water	Mixture		Z-		Zeta	
Sample	Concentrati on (mg/ml)	Volum e (ml)	Volum e (ml)	Startin g pH	Fina l pH	diamete r (nm)	PDI	potentia l (mV)	Remar k
- CUE- DEAE - T -	4	1	10	4.2	6	125±2	0.17 7	48.3±2. 3	
	4	1	10	4.2	7	130±4	0.11 5	46.3±0. 6	
	4	1	10	4.2	8	189±2	0.14 8	26.3±1. 0	
	2	1	10	4.2	7	99±1	0.11	36.5±0. 7	dialyse d
	4	1	10	4.2	7	113±1	0.17 1	39.6±1. 0	dialyse d
	6	1	10	4.2	7	151±2	0.11 8	38.6±1. 0	dialyse d
CUE- DMAE T -	4	1	10	4.5	6	178±2	0.11	46.8±1. 3	
	4	1	10	4.5	7	177±1	0.10	48.8±0. 1	
	4	1	10	4.5	8	177±2	0.11 5	37.1±0. 7	
	2	1	10	4.5	7	127±1	0.12 6	36.5±1. 8	dialyse d
	4	1	10	4.5	7	154±1	0.09	44.7±0. 9	dialyse d
	6	1	10	4.5	7	179±3	0.14 8	40.7±0. 6	dialyse d

**Table S2.** Characters of obtained NPs from CUE-DEAET and CUE-DMAET

## References

[1] a) A. Geissler, L. Q. Chen, K. Zhang, E. Bonaccurso, M. Biesalski, *Chem. Commun.* 2013, 49, 4962; b) X. T. Meng, J. B. Matson, K. J. Edgar, *Biomacromolecules* 2014, 15, 177; c) X. T. Meng, J. B. Matson, K. J. Edgar, *Abstr. Pap. Am. Chem. Soc.* 2014, 247.

[2] P. Dais, A. S. Perlin, Carbohydr. Res. 1988, 181, 233.