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Redox-responsive, reversibly fluorescent nanoparticles from sustainable cellulose derivatives

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Abstract

In comparison to single-stimuli responsive cellulose derivatives, multi-stimuli and reversibly responsive compounds from cellulose are still scarce. In this report, the fabrication of redox-controllable nanoparticles (NPs) from novel cellulose derivatives containing thiol groups and rhodamine spiroamide showing reversible fluorescence was described. The thiol groups were introduced into cellulose chains after the esterification by 3,3′-dithiodipropionic acid and further reductive cleavage of disulfide bonds. Then, rhodamine spiroamide was immobilized via thiol-ene reaction between cellulose thiopropionyl ester and rhodamine B methacrylamide. Obtained cellulose derivative containing rhodamine spiroamide (cellulose-RhBMA) could be transformed into NPs in aqueous medium and dissolved again via redox reactions on thiol groups. At the same time, cellulose-RhBMA exhibited reversible fluorescence that could be switched using pH (protons) or UV-illumination/heating as external stimuli. In total, we demonstrated the fabrication of redox-controllable NPs with reversible fluorescence, and a novel platform for the chemical modification of cellulose via thiol-ene reaction.

Introduction

Stimuli-responsive polymers attracted much attention in the last years, and most used extra triggers include light, pH, temperature and magnetic field.[1-6] Just as examples, poly(dimethyl acrylamide) (PDMAA) or polyglycerols containing nitrospiropyran groups change their physical properties in response to light,[7-9] synthetic polypeptides responsive to pH variation,[10] poly(N-isopropylacrylamide) (PNIPAM) responsive to temperature,[11] and cross-linked poly(vinyl alcohol) containing magnetite (Fe_3O_4) particles responsive to magnetic field.[12] However, most of stimuli-responsive polymers are hitherto still synthetic polymers, which contain corresponding functional groups for the stimuli-responsiveness.[5]

In comparison, stimuli-responsive polymers based on naturally occurring polysaccharides, in particular cellulose, are still limited to conventional stimuli, mostly pH and temperature.[13, 14] Cellulose, one of the most abundant native polysaccharides, consists of β-(1,4)-linked anhydroglucose units (AGUs) and contain three hydroxyl groups in each AGU. This chemical structure provides a platform for the derivatization with diverse functional groups.[15] Methyl-, ethyl- and hydropropylcellulose are probably the most common temperature-responsive cellulose derivatives.[13] Their hydrophobicity in the dissolved status increases with increasing temperature, and they show thermo-reversible gelation behavior. More studies focused on the grafting of stimuli-responsive polymer chains onto cellulose backbone,[16] e.g. with PNIPAM or poly(N,N-dimethyl aminoehtyl methacrylate) into hydroxylpropyl- or ethylcellulose, leading to pH- and thermo-sensitive copolymers.[17-19] By using this strategy, cellulose-based copolymers were adopted with the stimuli-responsiveness of synthetic polymers. Recently, fluorescent and light-responsive cellulose derivatives containing coumarin groups were reported and the coumarin moieties maintained responsive to UV-illumination.[20, 21]

In comparison to many other functional groups,[22] thiol moiety as a reactive group for facile thiol-ene groups has attracted until now more attention for the surface-modification of micro-/nanofibrillated cellulose,[23, 24] but much less attention for polymeric cellulose derivatives.[25, 26]

In this study, we report the first synthesis of multi-responsive cellulose derivatives via thiol-ene reaction, which can form redox-controllable nanoparticles (NPs) showing reversible fluorescence. Cellulose derivatives containing thiol groups were synthesized after the reaction with 3,3′-dithiodipropionic acid in ionic liquid, 1-butyl-3-methylimidazolium acetate (BMIMAc), and N,N-dimethylacetamide (DMAc). Then, rhodamine B methacrylamide was introduced into polymer chains via thiol-ene reaction on thiol groups. Synthesized cellulose

derivative, cellulose-rhodamine B methacrylamide (cellulose-RhBMA), formed NPs after the nanoprecipitation into water and these NPs can be dissolved or reconstructed again based on the redox property of thiol groups at cellulose chains. The rhodamine spiroamide immobilized onto thiol groups showed reversible fluorescence in response to pH (the presence of absence of protons) or UV-illumination/heating.

Experimental section

Materials

Microcrystalline cellulose with granule size of 50 μm, 3,3´-dithiodipropionic acid, rhodamine B base (97%), 1-butyl-3-methylimidazolium acetate (BMIMAc), aqueous ammonium thioglycolate solution (AmTG, 60%), ethylenediamine and methacryloyl chloride were obtained from Sigma-Aldrich (Steinheim, Germany). 1,1´-carbonyldiimidazol (CDI, >97%) and 1,3-propanedithiol (PDT) were purchased from Merck (Darmstadt, Germany) and triethylamine from Fischer Scientific (Loughborough, UK). Other chemicals are all of analytical grade and used without further treatment. Dialysis membrane with a molecular weight cut-off of 3500 was received from VWR International GmbH (Darmstadt, Germany).

Synthesis of thiolated cellulose (thiolcellulose 4) via dithiodipropionic ester of cellulose

Cellulose **1** (1 g, 6.17 mmol) in 50 mL BMIMAc was heated to 100°C to dissolve the cellulose. Then, 80 mL DMAc was added to the solution. The mixture was cooled to 80°C, the solution of 3,3´-dithiodipropionic acid **2** (12.97 g, 61.73 mmol) and CDI (5 g, 30.87 mmol) in 40 mL DMAc was added to the mixture. The mixture was allowed to react for 22 h at 80°C under stirring. The product was precipitated in 500 mL ethanol, centrifuged and the solid was washed with ethanol. Then, the product was dissolved in 50 mL water, filtered, dialyzed in deionized water and freeze-dried, leading to dithiodipropionic ester of cellulose (Yield: 1.2 g). The dithiodipropionic ester of cellulose (1 g dissolved in 60 ml water) was further reduced by 10 g ammonium thioglycolate aqueous solution (60%) at RT for 3 h. Then, the solution was precipitated in ethanol (400 ml) and the product was collected via centrifugation. After that, the precipitate was purified via dissolution in water, precipitation in ethanol and followed washing with acetone (2×50 ml). Finally, white powder was obtained after the removal of ethanol at RT, leading to thiolcellulose **4** (Yield: 0.68 g).

Synthesis of cellulose-rhodamine B methacrylamide (cellulose-RhBMA, 5)

Rhodamine B methacrylamide (RhBMA) **S3** was synthesized in two steps from rhodamine B as reported before (Scheme S1).[27, 28] Then, RhBMA was introduced into cellulose chains via thiol-ene reaction on the thiol groups within thiolcellulose **4**. Freeze-dried solid (0.5 g) in 30 ml DMSO was mixed with RhBMA (**3**, 0.48 g) and triethylamine (0.28 ml) at 50°C for 48 h. Then, the reaction was stopped by adding 250 ml THF and the precipitate was collected via centrifugation. After repeated dissolution in DMSO and precipitation using THF, the DMSO-soluble product **5a** was obtained after washing with THF (2×30 ml) and acetone (3×30 ml) before drying at 60°C (Yield: 0.4 g). Freshly synthesized **5a** was further reduced using ammonium thioglycolate aqueous solution (60%) at RT and precipitation in acetone, leading water-soluble **5b**.

Fabrication of NPs from cellulose-RhBMA (5a/5b)

5a was dissolved in DMSO at the concentration of 5, 10, 20 and 25 mg/ml. Then, 1 ml of each solution was dropped into 10 ml water. After 30 min, the mixture was dialyzed in water. To show the revisable dissolution and formation of NPs, 0.5 ml ammonium thioglycolate aqueous solution (60%) was added into 3 ml NPs suspension of **5a** (2 mg NPs/ml water), and the NPs suspension turned clear, indicating the formation of water-soluble **5b**. After the dialysis in water, the solution was diluted to 6 ml (with the concentration of 1 mg/ml). To 2 ml of this solution, 100 µl DMSO and 20 µl PDT were added. After 15 min ultrasonic treatment, the NPs suspension was dialyzed in water.

Characterization

Elemental analysis. The contents of carbon, hydrogen and nitrogen were determined with Elemental Analyser vario EL III CHN from Elementar (Hanau, Germany).

FTIR spectroscopy. FTIR spectroscopy was conducted on Spectrum One FTIR Spectrometer (PerkinElmer, Massachusetts, USA) at room temperature between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1}. The samples were measured twice per 16 scans and an average spectrum was then generated for each sample.

NMR spectroscopy. The liquid-state ^{13}C and ^{1}H **NMR** spectra of samples in D$_2$O or deuterated DMSO were recorded at RT on Bruker DRX 500 spectrometer (Bruker, Biospin GmbH,

Ettlingen) with a frequency of 125.7 MHz, 30° pulse length, 0.88 s acq. time and a relaxation delay of 0.4 s. Scans of 10000 and 80 were accumulated for ^{13}C and ^{1}H NMR spectroscopy, respectively.

Dynamic light scattering (DLS). DLS measurements were performed on Zetasizer Nano ZS (Malvern Instruments GmbH, Herrenberg, Germany) using 5 mW laser with the incident beam of 633 nm (He-Ne laser). The NPs suspensions were diluted with DI water to a concentration of ~0.04 mg/ml. 1 ml of suspension in quartz cuvette (Starna, Pfungstadt) were measured for three times with 10 runs for every measurement.

Fluorescence microscope. Fluorescence microscopic images were captured on an Olympus BX60 fluorescent microscope (Olympus Deutschland GmbH, Hamburg, Germany) equipped with an Olympus XM10 camera. The excitation and emission wavelength were 541 and 572 nm, respectively. An exposure time of 500 ms was used.

Fluorescence spectroscopy. Fluorescence spectroscopic measurements were carried out on a fluorescence spectrometer TIDAS S 700/ CCD UV/NIR linked with a monochromatic light source TIDAS LSM (J&M Analytik AG, Essingen, Germany). The whole system was processed using the TIDAS-DAQ software version 2.39 (J&M Analytik AG). The excitation wavelength of 540 nm, an acquisition time of 500 ms and an accumulation of 100 scans were used. The solution with the concentration of 20 mg **5a**/ml DMSO was used for the measurements. For the measurement in response to pH, 50 µl aqueous HCl or NaOH (5 wt.%) were added in the solution of **5a**. Quartz cuvettes (Type 3, from Starna GmbH, Pfungstadt, Germany) were used and cleaned with DMSO and acetone as well as dried with nitrogen gas before each measurement.

Results and Discussion

One major reason for scarce multi-stimuli responsive cellulose derivatives is the complicated multi-step synthesis for the introduction of stimuli-responsive functional groups into cellulose chains. In order to introduce a general functional group into cellulose backbone that could be further used for the coupling of versatile groups, thiol moiety was chosen due to its highly specific reaction with carbon-carbon double bond and mild reaction conditions, e.g. UV-illumination at room temperature.[29, 30] For this purpose, 3,3′-dithiodipropionic acid (DTDPA) was used to esterify OH-groups in AGUs for the introduction of protected thiol groups. The

esterification of OH-groups by DTDPA was carried out in 1-butyl-3-methylimidazolium acetate (BMIMAc)/DMAc solution and catalyzed by 1,1′-carbonyldiimidazol (CDI) (Scheme 1).[31, 32] The introduction of DTDPA into cellulose chains was confirmed by FTIR spectroscopy (Figure S1) and the disulfide groups within DTDPA can be cleaved using active reducing agents, such as ammonium thioglycolate. After that, thiolcellulose with thiol groups along cellulose chains was obtained (Scheme 1) and the degree of substitution ascribed to thiol groups was determined to be 0.62 based on elemental analysis.

The presence of thiol groups provides the feasibility to further react with versatile functional groups containing C=C-bonds via thiol-ene reactions, in particular in our study, rhodamine B methacrylamide (Scheme 1, *ii*). Rhodamine is a photostable fluorescent dye with wide potential applications in biosensing and imaging.[33, 34] In order to immobilize rhodamine spiroamide onto thiol groups in thiolcellulose **4**, rhodamine spiroamide in ring-closed form was decorated with methacrylamide groups (Scheme S1).[27, 28] After the thiol-ene reaction, obtained cellulose-RhBMA **5a** shows clearly the presence of both rhodamine spiroamide and cellulose backbone according to ^{1}H, ^{13}C NMR and FTIR spectrum (Figure 1 & S3). Moreover, the presence of signals at 173, 99.5 and 63 ppm ascribed to C in carboxyl groups, C1′ as well as C6′ indicate the derivatization of the hydroxyl groups at C6 and C2 positions by thiopropionic acid.[32, 35, 36] The degree of substitution ascribed to rhodamine groups was calculated to be 0.12 based on elemental analysis, indicating that about 20% of total thiol groups were involved in the thiol-ene reaction.

5a is readily soluble in DMSO, but not in water. By the addition of aqueous solution of ammonium thioglycolate (60%) into the DMSO solution of **5a**, water-soluble, reduced **5b** was obtained. Thus, the non-solubility of **5a** in water is due to the presence of disulfide linkages.[25] A competing reaction as the disulfide formation took place during the thiol-ene reaction, due to the oxidizing feasibility of thiol groups by DMSO/O$_2$.[25, 37]
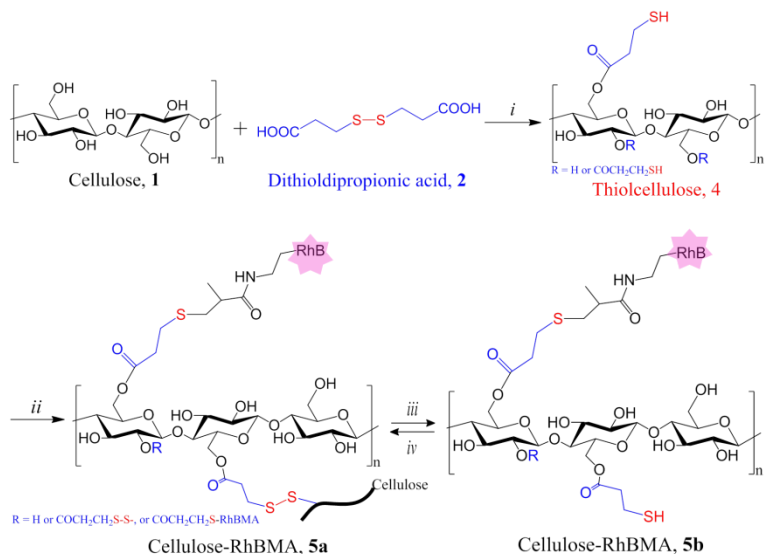
Scheme 1. Schematic illustration for the synthesis of cellulose-RhBMA, **5a/5b**. *i*: (1) 1-butyl-3-methylimidazolium acetate (BMIMAc), DMAc, CDI, 80°C, 22 h; (2) aqueous ammonium thioglycolate (60%), 3 h; *ii*: rhodamine B methacrylamide (RhBMA, **S3**), DMSO, 50°C, 48 h; *iii*: reduction in DMSO with aqueous ammonium thioglycolate (60%), 3 h. *iv*: oxidation by dissolution in DMSO.
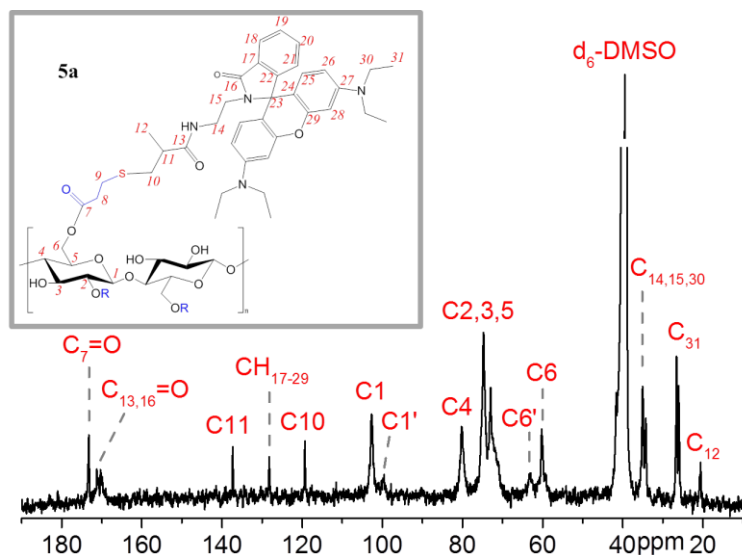

Figure 1. ^{13}C NMR spectrum of **5a** in d$_6$-DMSO (^{1}H NMR spectrum in Figure S3).

The solubility of **5a** in DMSO but not in water allows the formation of NPs from **5a** in water via nanoprecipitation.[38-40] The addition of the DMSO solution of **5a** into excess water led to a stable, milky NPs suspension (Movie S1). The average diameters of these NPs were measured to be

between 180 and 360 nm, depending positively on the concentrations of the **5a** solutions (Figure 2). Due to the redox feasibility of the disulfide groups, these NPs could be dissolved again via the addition of a reducing agent, such as ammonium thioglycolate or dithiolthreitol (Movie S2). The reduction and thus the cleavage of the disulfide bonds of **5a** led to water-soluble **5b** (Scheme 1). **5b** is water-soluble due to the presence of thiol groups along cellulose chains. These thiol groups can be further oxidized using oxidizing agents for thiol groups including O_2 gas and aqueous $NaClO_2$,[25] resulting in **5a** containing disulfide linkages. However, these oxidations did not lead to the formation of NPs, but only white flocculants. In contrast, if 1,3-propanedithiol (PDT) in DMSO was added into the aqueous solution of **5b**, NPs could be reconstructed again after the removal of DMSO. Nevertheless, these NPs from a **5b** solution of 1 mg/ml exhibited a large average diameter of 384±14 nm, compared to the NPs from **5a** solutions of higher concentrations after the nanoprecipitation (Figure 2b). Thus, the NPs from cellulose-RhBMA can be reversibly dissolved and reconstructed again by using corresponding redox-reaction (Figure 3).
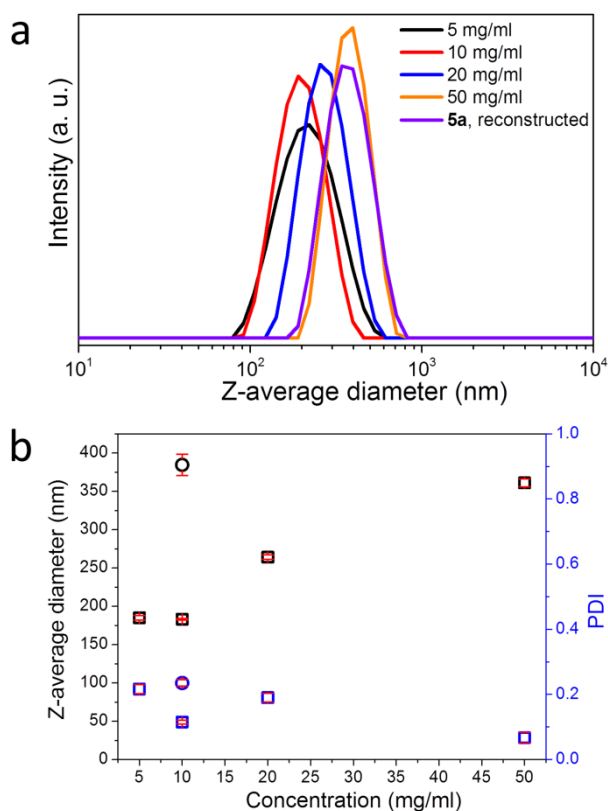

Figure 2. (a) DLS curves of aqueous NPs suspensions of cellulose-RhBMA **5a** from its solutions in DMSO at diverse concentrations as well as reconstructed NPs. (b) Z-average diameters and

PDI of NPs. Square: from solution of **5a** in DMSO and circle: reconstructed NPs from dissolved **5b** in water using 1,3-propanedithiol/DMSO. The red lines are error bars.
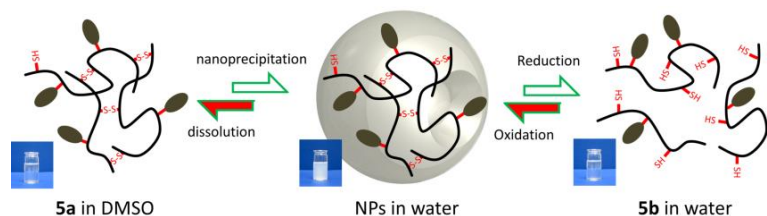

Figure 3. Schematic representation of the formation and dissolution of NPs via nanoprecipitation/dissolution of **5a** or oxidation/reduction of **5b**. The insets show representative images.

The fluorescence of **5a** dissolved in DMSO can be altered by changing the pH of its solution via addition of low amount of aqueous HCl or NaOH.[28] At acidic condition, strong fluorescence is visible due to the presence of the intensive emission signal at 590 nm ascribed to rhodamine, while very weak fluorescence is observed under alkaline condition according to the fluorescence spectroscopic analysis (Figure 4a). After drying, **5a** with rhodamine spiroamide in ring-closed form is a light-yellow compound showing weak fluorescence, while UV-illumination of **5a** led to the emergence of pink color and thus stronger fluorescence (Figure 4b). A further heating treatment led to the decrease of the color intensity and accompanying fluorescence. The reason is the switching ability of rhodamine spiroamide between ring-closed form (weakly fluorescent) and ring-open form (strongly fluorescent) depending on the external stimuli, e.g. UV-illumination, heating or pH.[28, 41] In comparison, the switching of the fluorescence of **5a** in DMSO could not be conducted using UV and heating as external stimuli (Figure S4). Reduced **5b** dissolved in water also did not show alteration of the fluorescence after the UV-illumination (Figure S5). This effect is due to the presence of preferential open ring of rhodamine spiroamide while dissolved in polar solvents as DMSO or H_2O.

As well, the NPs of **5a** were also endowed with the reversible fluorescence, which is displayed using fluorescence microscopy. By nanoprecipitating DMSO solution of **5a** into water and followed drying, obtained NPs with non-activated rhodamine exhibits very low fluorescence (Figure 5a). As further illustrated with the fluorescence microscopic analysis, the fluorescent intensity of dried **5a** NPs could be switched via UV-illumination and heating at 130°C (Figure

5a-d). After UV-illumination at 365 nm for 30 min, the fluorescence becomes stronger, while subsequent 30 min treatment at 130°C resulted in weaker fluorescence. The switching of the fluorescence intensity can also be realized after shorter time, such as 10 min UV-illumination or heating (Figure S6). Thus, by applying these external stimuli, the fluorescence intensities of the NPs can be reversibly adjusted (Figure 5e). It should be noted that dried **5a** already exhibited slight pink color and associated fluorescence. Further switching using UV-illumination and heating led to steadily lower switching feasibility. Furthermore, the UV-illumination and heating are effective stimuli for the samples at dried status, while they could not significantly change the fluorescence of dissolved samples. The fluorophores with switchable fluorescence, such as rhodamine B and spiropyrane, prefer a particular chemical structure if dissolved in a certain solvent, e.g. they demonstrate strong fluorescence if they are dissolved in polar solvents.[42, 43] Nevertheless, the pH value or precisely the presence or absence of protons is another stimulus for switching the fluorescence of dissolved fluorophore.

Moreover, these multi-responsive NPs from biocompatible and sustainable cellulose are promising candidates for biomedical sensing and imaging.[44, 45] In particular, they can potentially be used for site-specific detection and delivery of drugs.[6, 46-48]
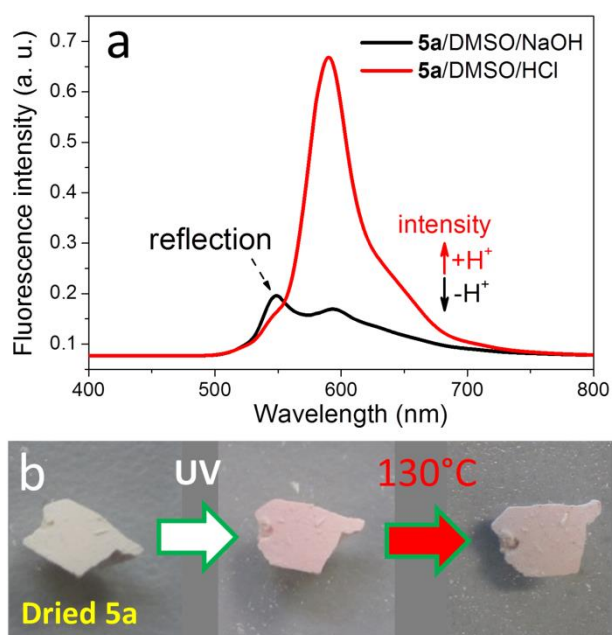

Figure 4. Reversible fluorescence of **5a**. (a) Fluorescence spectra of **5a** in DMSO with the addition of 50 µl aqueous HCl or NaOH (5 wt.%). (b) Photo images of freshly dried **5a**, UV-illuminated **5a** (at 365 nm for 30 min) and subsequently heated **5a** (at 130°C for 30 min).
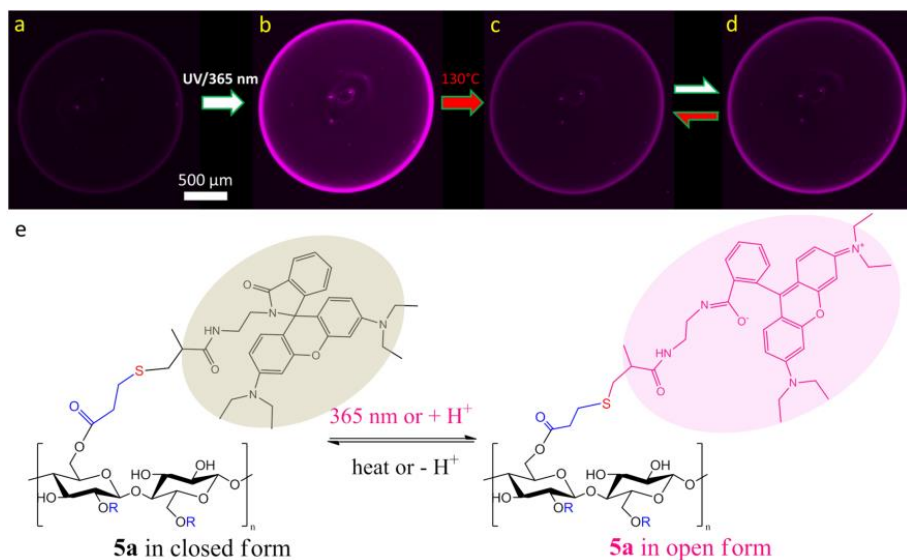
Figure 5. Fluorescence microscopic images of dried NPs from **5a**: (a) freshly prepared and dried NPs, (b) after UV-treatment at 365 nm for 30 min, (c) the same NPs after heating at 130°C for 30 min. (d) the same NPs after the second UV-treatment at 365 nm for 30 min as well as schematic illustration of the reversibility between weakly and strongly fluorescent NPs (short-time treatments in Figure S6). Scale bar: 500 µm. (e) Schematic representation of the structural change of **5a** in response to corresponding treatments.

Conclusion

In summary, we reported the synthesis of novel, multi-stimuli responsive and reversibly fluorescent cellulose derivatives containing thiol groups and rhodamine spiroamide, which can form NPs or be dissolved again under redox-controllable conditions. The thiol groups were introduced into cellulose chains after an esterification with 3,3′-dithiodipropionic acid, which provide a platform for further modifications via thiol-ene reaction, and in the present study, rhodamine B methacrylamide. Cellulose-RhBMA **5a** containing disulfide groups was transformed into NPs via nanoprecipitation of its DMSO solution into water. The NPs could be dissolved or reconstructed through the reduction or oxidation, respectively. The rhodamine spiroamide endows the cellulose-RhBMA **5a** and the NPs reversible fluorescence, in response to UV-illumination/heating or pH (presence or absence of protons). These multi-responsive NPs from biocompatible and sustainable cellulose with reversible fluorescence are of particular interest for the biomedical sensing and imaging. Moreover, the facile thiol-ene reaction can be applied for the construction of novel cellulose derivatives.

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Table of content

Multi-stimuli responsive and reversibly fluorescent compounds from sustainable cellulose were synthesized after the introduction of thiol and rhodamine spiroamide groups.