Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Redox-responsive, reversibly fluorescent nanoparticles from sustainable cellulose derivatives

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Keywords: cellulose, redox, thiol, reversible, fluorescence

Movies.

Movie S1. Demonstration of the nanoprecipitation process for the fabrication of nanoparticles from **5a** by adding 1 ml, and after shaking another 1 ml, water to the 0.5 ml DMSO solution of **5a**.

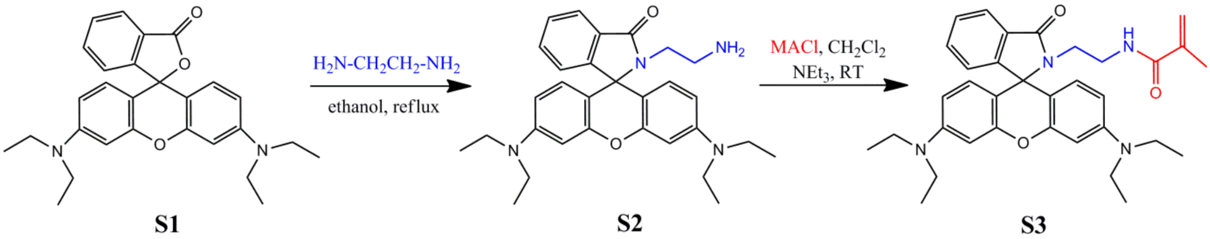
Movie S2. Demonstration for the dissolution of nanoparticles from **5a** by adding 1 ml aqueous ammonium thioglycolate solution (60 wt.%) to 3.5 ml nanoparticle suspension.

Methods.

Synthesis of rhodamine methacrylamide.

Rhodamine B methacrylamide (RhBMA) was synthesized as described before with a few modifications.[1, 2] **Rhodamine, S1** (1.15 g, 2.6 mmol) and ethylenediamine (2.03 g, 33.8 mmol) were dissolved in EtOH (100 mL) and refluxed for 16 h. The solvent was removed by evaporation, and the residue was dissolved in an aqueous HCl solution (1M, 100mL). Aqueous NaOH solution (1 M) was added to the solution under stirring until the beginning of an appearance of pink precipitate. Then, the mixture was filtered; the solid aminoethyl rhodamine **S2** was washed with water, and dried in vacuum. Yield: 52.5%.

S2 (0.68 g, 1.36 mmol) was dissolved in dichloromethane (5 mL) under N_2 followed by the addition of triethylamine (0.5 mL, 3.26 mmol). Methacryloyl chloride (0.26 mL, 2.72 mmol) in dichloromethane (2 mL) was added to the solution at 0℃; after the addition, the mixture was kept at RT for 18 h. After that, the mixture was washed with distilled water (5x30 mL), saturated Na_2CO_3 (3x30 mL), followed by drying with Na_2SO_4, and the solvent was evaporated under vacuum. The residue was dissolved in ethyl acetate, filtered and dried under vacuum. Then, RhBMA **S3** was obtained as slightly pink solid. Yield: 46.7%.



Scheme S1. Schematic representation of the synthesis of RhBMA (S**3**) from rhodamine (S**1**). MACl: methacryoloyl chloride, NEt_3: triethylamine.

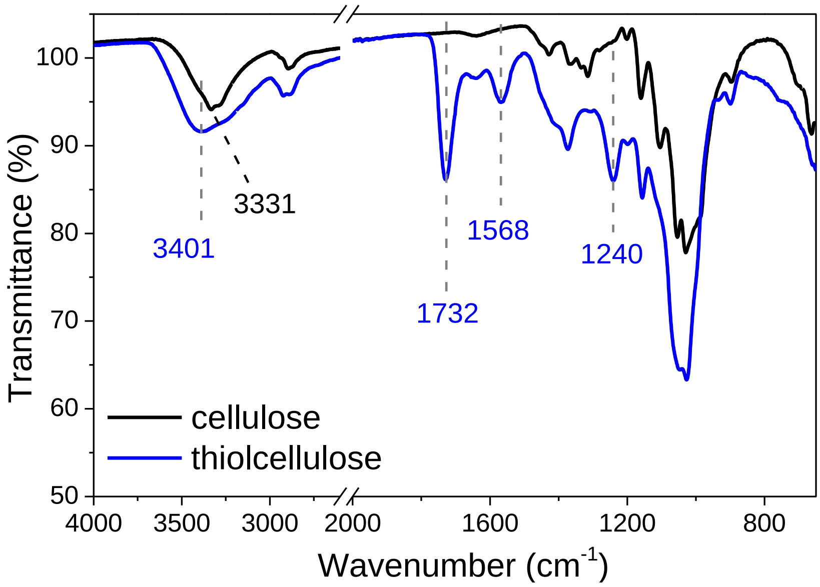


Figure S1. FTIR spectra of cellulose, cellulose-DTDPA and thiolcellulose **4**.

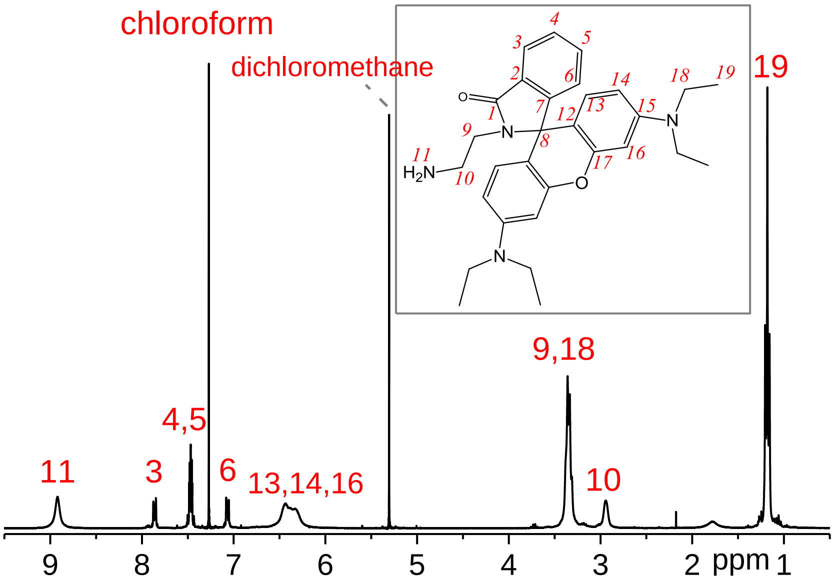


Figure S2. ^{1}H NMR spectrum of aminoethyl rhodamine **S2**.

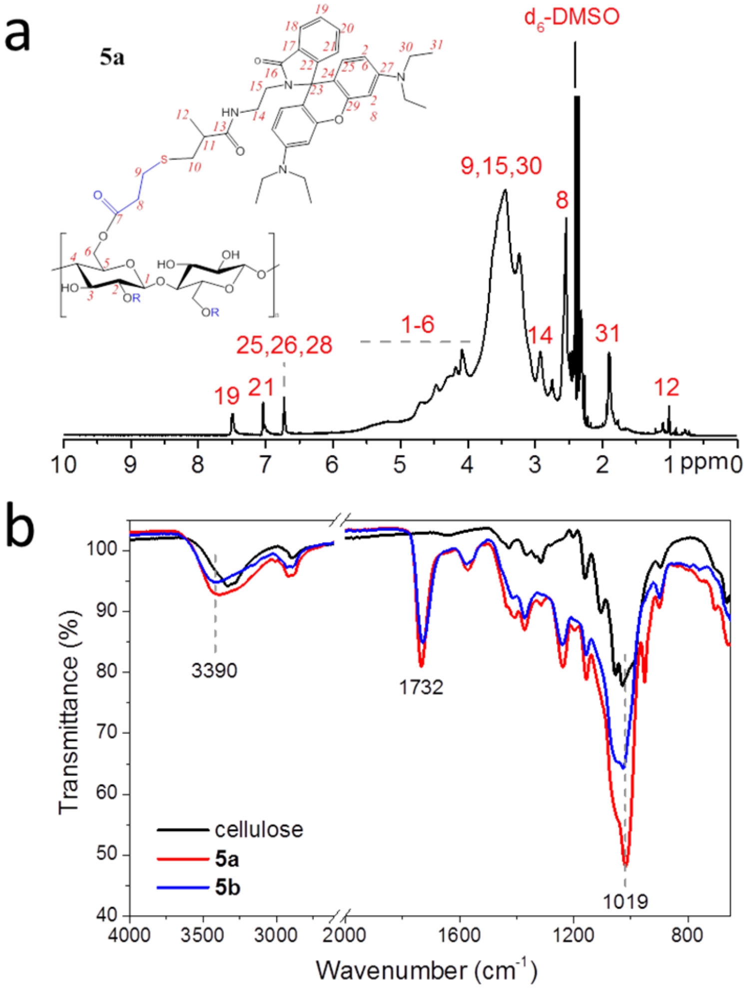


Figure S3. (a) ^{1}H NMR spectrum of **5a** in d$_6$-DMSO. (b) FTIR spectra of cellulose and cellulose-RhBMA as oxidized form **5a** and reduced form **5b**.

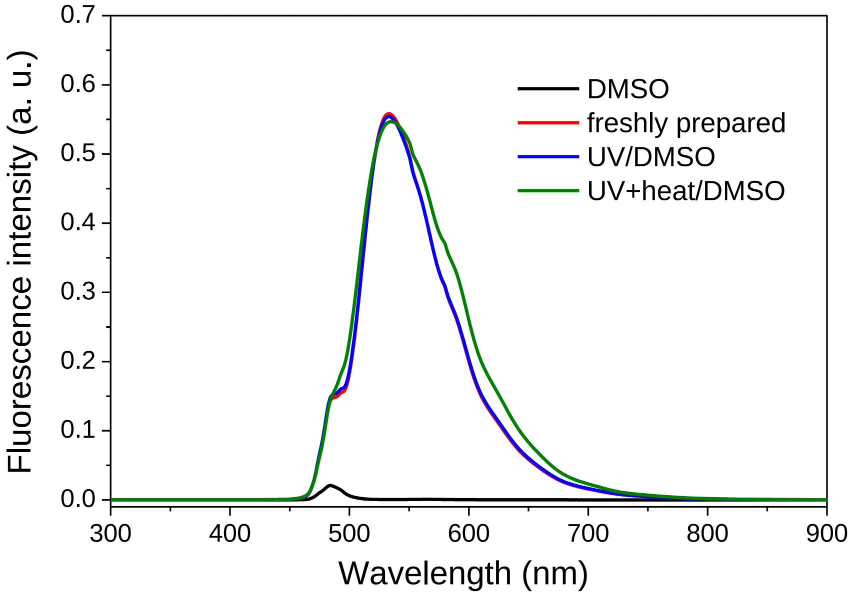


Figure S4. fluorescence spectroscopic measurements of cellulose-RhBMA **5a** in DMSO after diverse treatments.

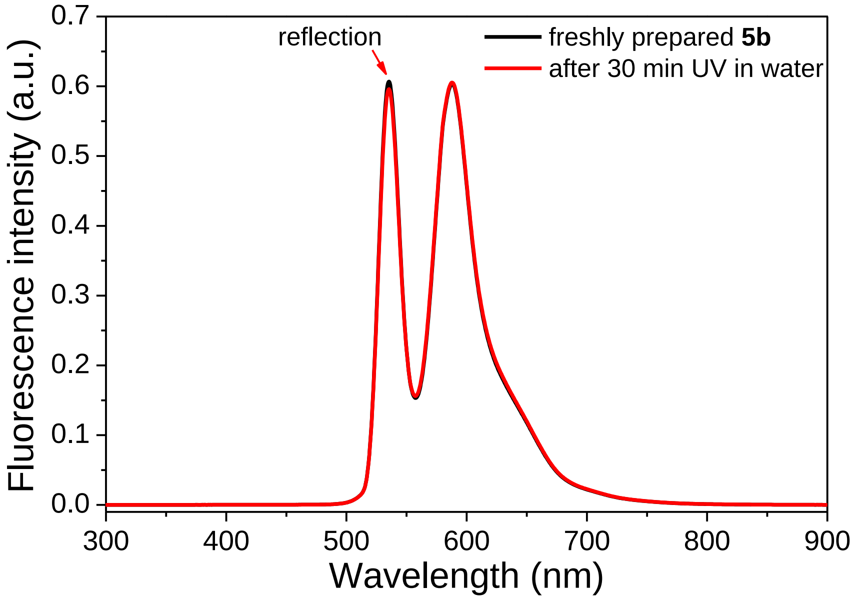


Figure S5. fluorescence spectroscopic measurements of cellulose-RhBMA **5b** in water before and after 30 min UV-illumination.

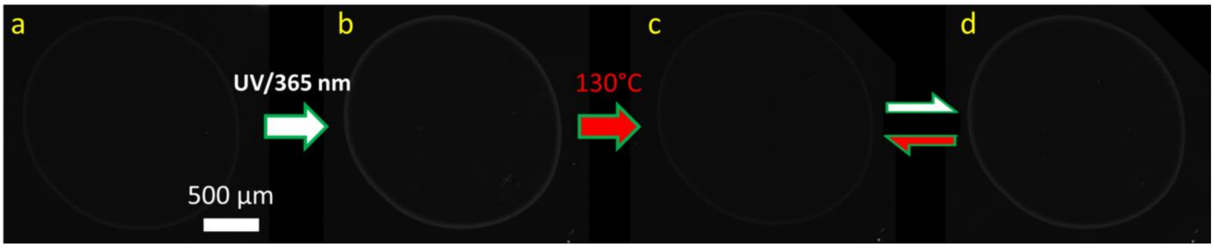


Figure S6. Fluorescence microscopic images of dried nanoparticles from cellulose-RhBMA **5a**: (a) freshly prepared and dried nanoparticles, (b) after UV-treatment at 365 nm for 10 min, (c) the same nanoparticles after heating at 130°C for 10 min. (d) the same nanoparticles after the second UV-treatment at 365 nm for 10 min as well as schematic illustration of the reversibility between weakly and strongly fluorescent nanoparticles. Scale bar: 500 µm.

References

1. C. G. Schäfer, M. Gallei, J. T. Zahn, J. Engelhardt, G. P. Hellmann and M. Rehahn, *Chem. Mater.*, 2013, **25**, 2309-2318.
2. Y. Shiraishi, R. Miyamoto, X. Zhang and T. Hirai, *Org. Lett.*, 2007, **9**, 3921-3924.