Supplementary Information

Shine-Through Luminescent Wood Membranes

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EXPERIMENTAL

Materials

Dibenzoylmethane (DBM, 98 %), triethylamine (Et_3N, ≥ 99.5 %), europium(III) nitrate pentahydrate (99.9 %), sodium metasilicate, magnesium sulphate (≥ 99.5 %, anhydrous), ethylenediaminetetraacetic acid (EDTA, ≥ 98.5 %), absolute ethanol (> 99.8 %) and acetone (≥ 99.9 %) were purchased from Sigma Aldrich. Sodium hydroxide aqueous solutions (0.1 M and 1 M) were purchased from VWR Chemicals. Hydrogen peroxide (> 30 m%) was purchased from Fisher Scientific. Fluorescein (pure) was purchased from ACROS Organics. All chemicals were used as supplied by commercial sources.

Typical experimental protocols

Synthesis of EuD_3TEA

Europium dibenzoylmethide triethylammonium (EuD_3TEA) was synthesised according to the protocol reported by Fontenot *et al.* [1] Four equivalents (6 mmol) of dibenzoylmethane were dissolved in 35 mL of ethanol by heating in an Erlenmeyer flask, topped with a funnel to reduce evaporation of the solvent. After the solution almost reached the boiling point and the DBM fully dissolved, four equivalents (6 mmol) of triethylamine (Et_3N) were added. One equivalent (1.5 mmol) of europium (III) nitrate pentahydrate was dissolved in 4 mL of ethanol by heating and then added to the Erlenmeyer flask: the solution immediately turned bright yellow. The heating was turned off, the Erlenmeyer flask topped with a petri dish and left to slowly cool to room temperature. Yellow crystals, with strong red luminescence under UV light, formed on the bottom of the flask within 12 hours. They were collected and washed three times with ethanol, then dried under vacuum. A 10 mM EuD_3TEA solution was prepared dissolving the crystals in ethanol by heating and sonication.

Wood decolourisation

The protocol reported by Li *et al.* [3] was slightly modified. An aqueous solution containing the following chemicals: sodium metasilicate (3 m%), sodium hydroxide (3 m%), magnesium sulphate (0.1 m%), ethylenediaminetetraacetic acid (0.1 m%) and hydrogen peroxide (4 m%). The mass percent (m%) values are in relation to the mass of water used.

A typical decolourisation mixture contained: 600 mL deionised water, 18 g sodium metasilicate, 18 mL of 0.1 M sodium hydroxide solution, 0.6 g magnesium sulphate, 0.6 g ethylenediaminetetraacetic acid and 80 mL hydrogen peroxide solution. The sodium metasilicate is first dissolved by vigorous stirring, then the sodium hydroxide is added, followed by the magnesium sulphate and the ethylenediaminetetraacetic acid. Sonication helps to obtain a homogeneous solution. Finally, hydrogen peroxide is added. In a 1 L beaker, a magnetic stirrer is surmounted by a metal mesh cage to hold the wood samples to be decolourised. The decolourisation mixture is then heated to 65 °C. The wood samples are removed after complete decolourisation (ca. 1-2 hours, depending on the wood species and size of the wood samples), washed thoroughly with deionised water and left in 3 L water. The water is changed from time to time until colourless and of neutral pH.

Oven-drying the water-soaked wood samples can result in cracks and warping. Therefore, a solvent exchange from water to acetone is needed, by equilibrating the samples in the following solutions: 1:1 (by volume) water and ethanol (EtOH), EtOH, EtOH, 1:1 (by volume) EtOH and acetone, acetone and acetone. The solvent is exchanged every 12 h. After the final step, the wood pieces are left to dry in ambient conditions before being fully dried under vacuum (approx. 12 mbar) in a desiccator.

Wood functionalisation with EuD_3TEA

The native and decolourised wood pieces were functionalised either by dropping 10 µl of the 10 mM EuD_3TEA solution on top with a pipette, or by spraying the solution (500 µl) with a spray bottle.

Characterisation techniques

Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectra were acquired with a Bruker Tensor27. Light transmission was measured with a Perkin Elmer Lambda 605 UV-Vis Spectrophotometer with the 150 mm integrating sphere. Fluorescence spectra were recorded with an Agilent Cary Eclipse spectrofluorometer. Mechanical properties were determined with a Zwick Roell Z010. Accelerated ageing was performed using a Hönle UVAcube 400 equipped with a sol500 lamp and a H2 filter, with emission maxima at 400 nm and 500 nm (according to the manufacturer, under these conditions ageing is accelerated by up to 9 times compared to normal sunlight exposure).

To illustrate the shine-through effect, a UV lamp with a main emission wavelength of 395 nm was used. The UV lamp used for illumination from the top had an emission wavelenght of 366 nm. The UV LED used for the demonstrator had a main emission wavelength of 375 nm.

Construction of the demonstrator

The demonstrator consists of a 4x4 cm^2 native spruce cross-section base plate on which a small wooden stick is placed to hold the UV LED approximately in the centre of the cube (**Figure SA,B**). The two wires are connected to a 3.6 V lithium-ion battery (not shown in the image) and are fed through a small gap located at the back of the demonstrator. Like the base plate, the four non-functionalised faces on the top are made from a 4x4 cm^2 native spruce cross-section pieces with a thickness of *ca.* 2.4 mm, and lined with aluminium foil (**Figure SC**). Finally, the front face is put in place (in the case of **Figure SD** an EuD_3TEA-functionalised decolourised wood cross-section with a thickness of 1.43 mm, while in the manuscript a EuD_3TEA-functionalised native wood cross-section with a thickness of 1.59 mm is shown) by attaching it to the front using double-sided tape. The functionalised decoloured face leads to a higher emission of the face, but consequently, some red light is also transmitted through the other, non-functionalised faces as the lining with the aluminium foil cannot fully prevent it.

Table S1. Summary of the specimen thickness for the transmission measurement.

Cut	Native/decoloured	Thickness [mm]
cross-section	native	1.49
	decoloured	1.47
tangential	native	1.08
	decoloured	1.07
radial	native	1.11
	decoloured	1.20

Table S2. Summary of the specimen thickness for the fluorescence shine-through quantification.

Cut	Native/decoloured	Thickness [mm]
cross-section	native	1.50
	decoloured	1.55
tangential	native	1.02
	decoloured	1.18
radial	native	1.02
	decoloured	1.07

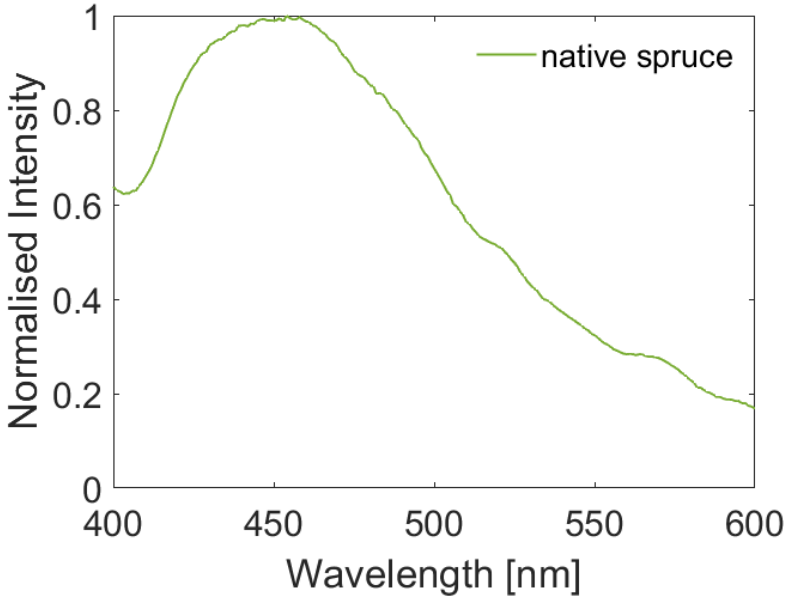

Figure S1. Intrinsic fluorescence of native spruce wood, due to its lignin content. [4]

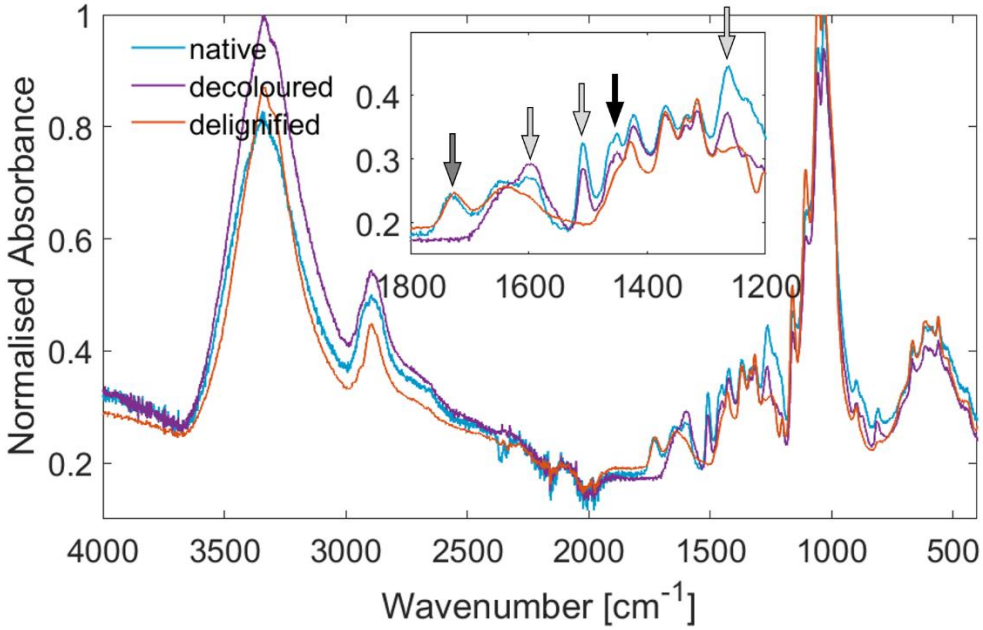

Figure S2. ATR-FTIR spectra of native (*full blue line*), decolourised (*full purple line*) and delignified (*full red line*) spruce wood. The main differences between the three samples are highlighted in the inset. The black arrow indicates an unidentified chromophore peak, the light grey arrows characteristic lignin peaks and the medium-grey arrow a peak assigned to carboxylic acid groups.

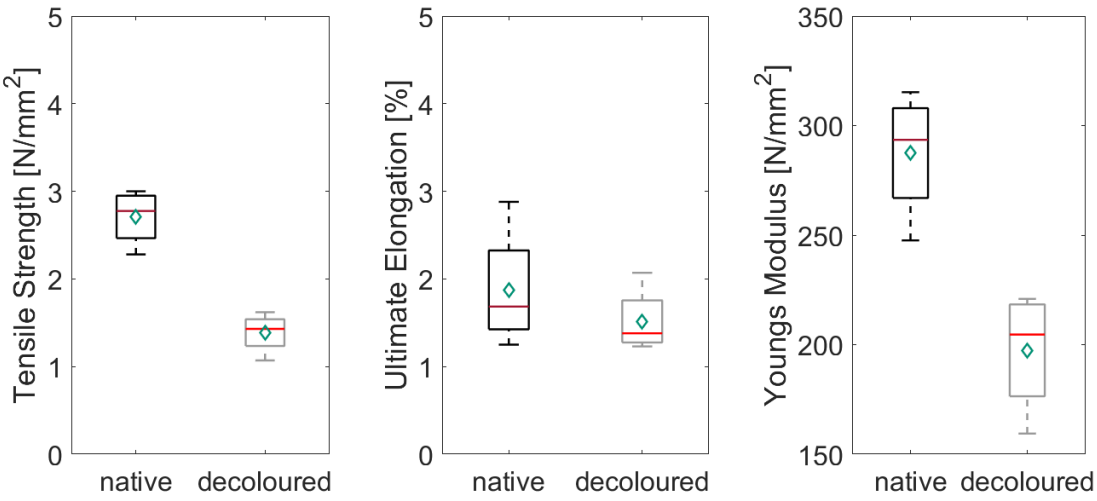

Figure S3. Mechanical properties of native and decolourised spruce membranes (measured in the tangential direction): tensile strength (*left*), ultimate elongation (*centre*) and Young's modulus (*right*). The red line indicates the median value, while the upper and lower edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers indicate the most extreme values, and the blue rhombus indicate the mean values.

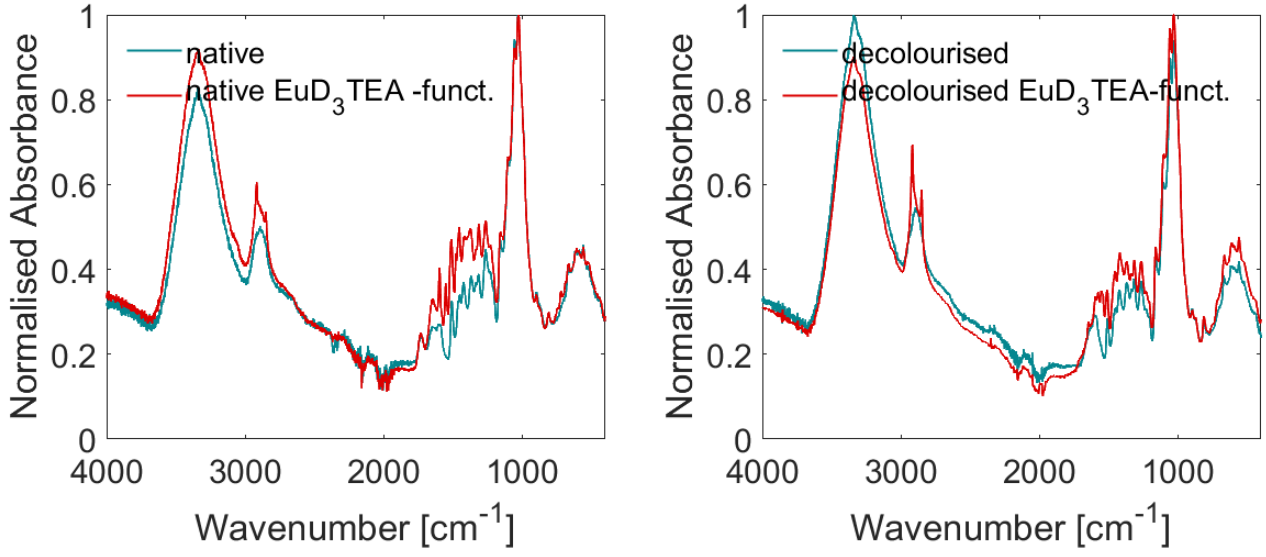

Figure S4. ATR-FTIR spectra of pristine and EuD_3TEA-functionalised (***A***) native spruce, (***B***) decolourised spruce.

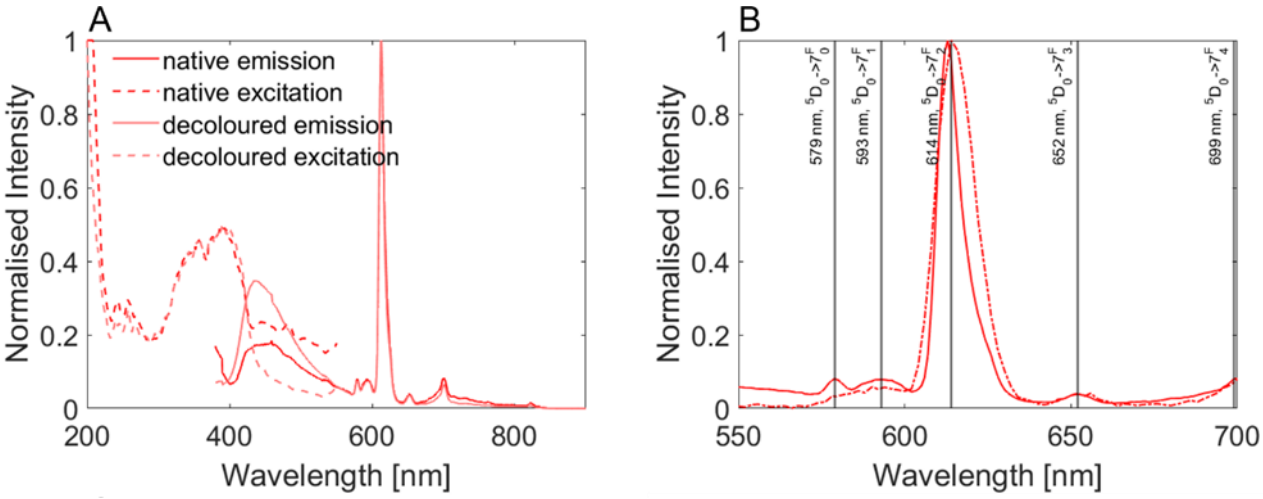

Figure S5. Emission and excitation spectra of EuD_3TEA-functionalised native and decolourised wood. (**A**) Fluorescence emission (full line, λ_{ex}= 340 nm) and excitation (dotted line, λ_{em}= 613 nm) spectra of EuD_3TEA functionalised native (*dark red line*) and decoloured (*faint red line*) and spruce. The excitation and emission spectra of both EuD_3TEA-functionalised native and decolourised wood are congruent, except for an emission at ~430 nm (from lignin) which is more intense for decolourised wood. [4] (**B**) Emission spectra of EuD_3TEA functionalised native spruce and the EuD_3TEA solution used for functionalisation. The peaks were assigned according to [5]

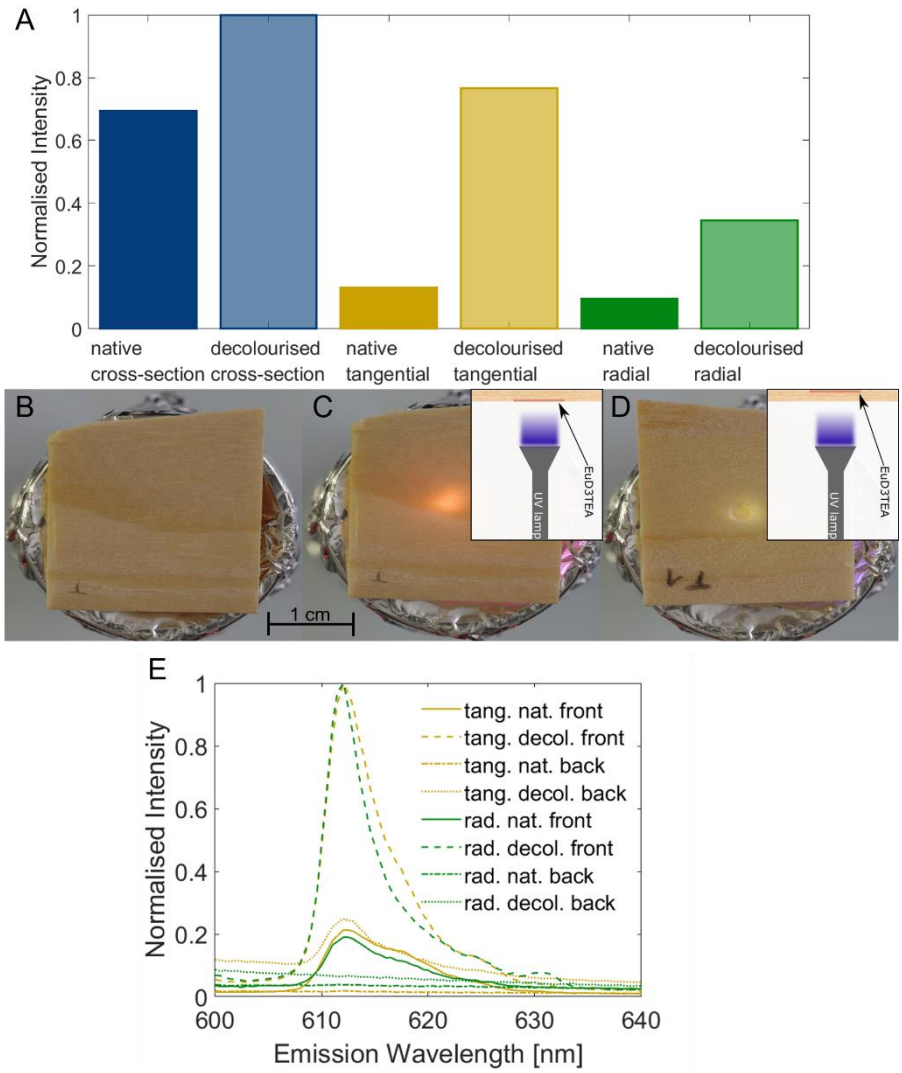

Figure S6. (***A***) Bar graph illustrating the shine-through fluorescence intensity for both native and decoloured cross-sections, tangential and radial cuts. The data correlates well with the light transmission results. The samples' thicknesses are in **Table S2**. (***B***, ***C***, ***D***) Photographs showing the shine through effect in a EuD_3TEA-functionalised spruce tangential cut (thickness 1.04 mm): (***B***) not illuminated, (***C***) functionalised side illuminated with UV light ("*front*"), (***D***) non-functionalised side illuminated with UV ("*back*"). The schematic drawings of the *front* and *back* configuration are also shown. (***E***) Quantification of the shine-through effect for native and decolourised tangential and radial cuts in the *front* and *back* configuration. Only the *front* configuration allows for sufficiently intense red light being emitted on the side facing the detector or eye. For the cross-section, there is no measurable difference due to the deeper distribution of the EuD_3TEA in the lumen (data not shown).

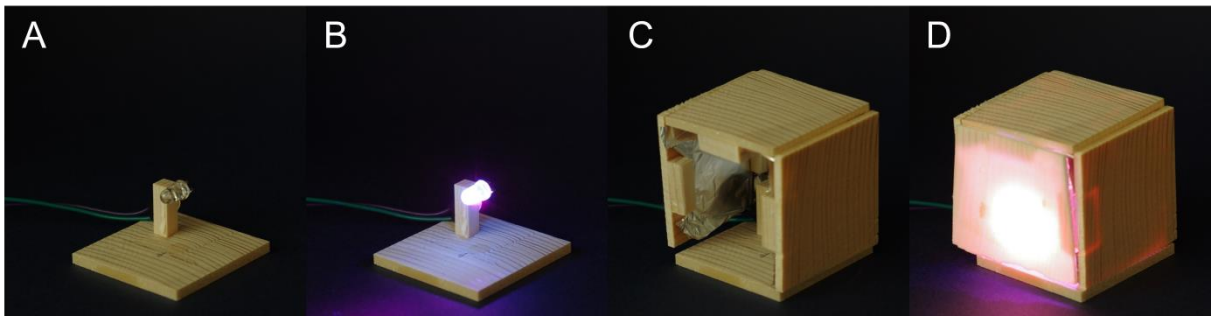

Figure S7. Detailed overview of the construction of the demonstrator. (***A***) UV LED (375 nm) placed approx. in the centre, wiring goes to an adjacent 3.6 V battery, (***B***) UV LED turned on, (***C***) the four non-functionalised faces of the demonstrator put in place to form a cube, shielded inside with aluminium foil, (***D***) EuD_3TEA-functionalised decolourised wood face (1.43 mm thick) illuminated from the inside.

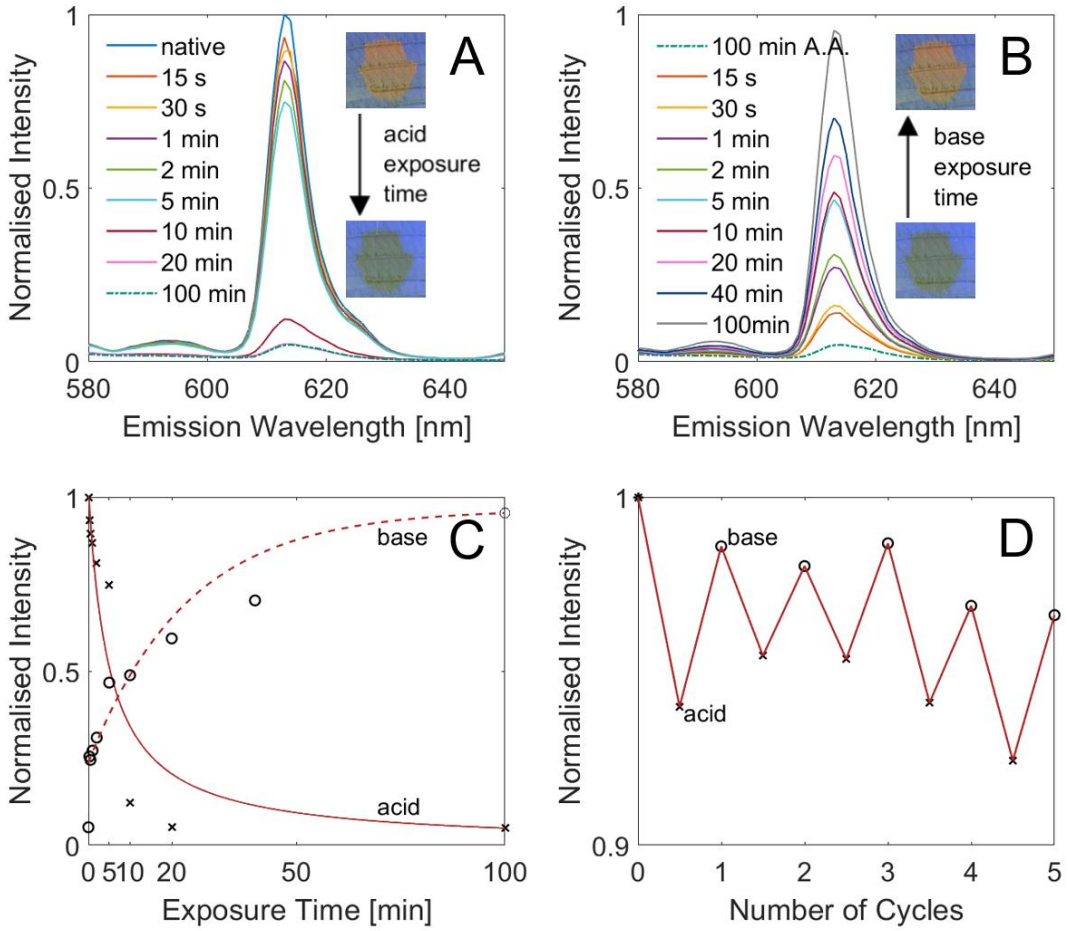

Figure S8. Fluorescence of EuD_3TEA-functionalised decolourised wood cross-sections exposed to acetic and alkaline vapours. (***A***) show the main emission peak of EuD_3TEA (~ 615 nm) in native and decolourised wood respectively as a function of time exposed to acetic acid (A.A.) vapour. (***B***) show the main emission peak of EuD_3TEA as a function of time exposed to Et_3N vapour. (***C***) show the intensity of the main emission peak plotted against the acetic acid (*crosses*) and Et_3N (*circles*) exposure time and fitted with an exponential approach (*full red line for acetic acid and dotted red line for Et_3N*). (***D***) show the intensity after alternating 1 min exposure to acetic acid (*cross*) and Et_3N (*circle*) vapours.

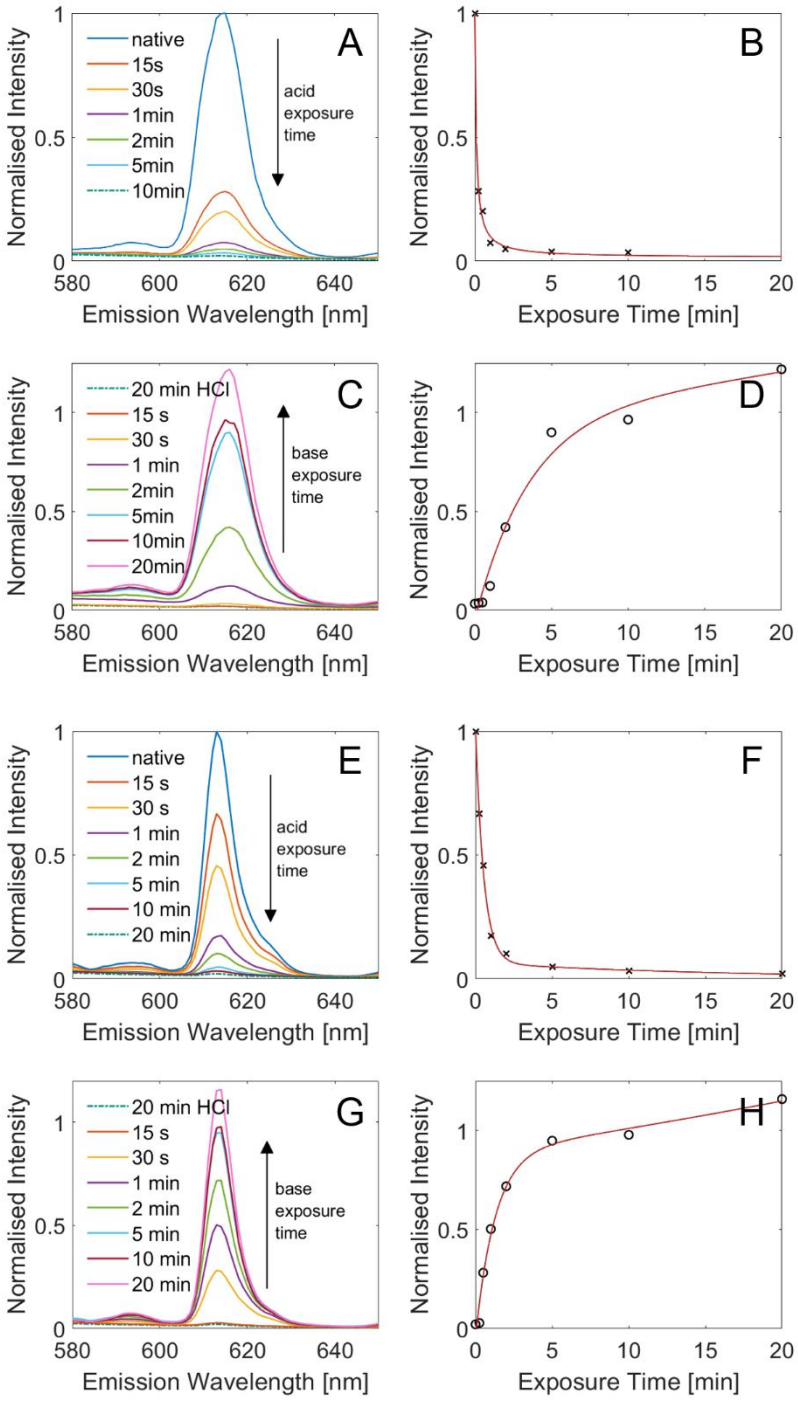

Figure S9. Fluorescence spectra of EuD_3TEA-functionalised native (**A**-**D**) and decolourised (**E**-**H**) wood cross-sections exposed to acidic (HCl (**A**,**E**)) and alkaline (NH_3 (**D**, **H**)) vapours for different times. The main emission peak is plotted against the exposure time to HCl (**B**, **F**) or NH_3 (**D**, **H**) and fitted with an exponential approach (*full red line*). With ammonia, the fluorescence intensity is increased beyond the value for the native sample by a factor of approx. 1.2, possibly because it partially substitutes to Et_3Nin the europium complex.

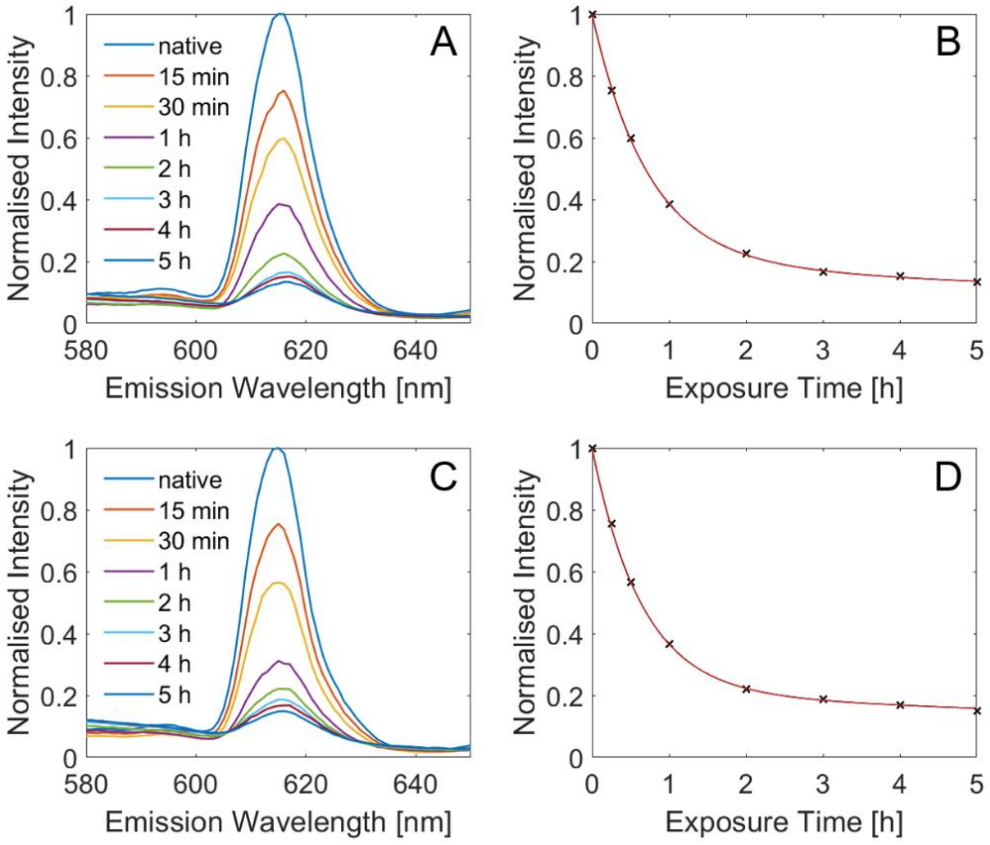

Figure S10. Photostability of EuD_3TEA-functionalised native (***A***, ***B***) and decolourised (***C***, ***D***) wood cross-sections after exposure to 1000 W m^{-2} UV light (main emissions at ~400 nm and ~500 nm). (***A***, ***C***) Fluorescence spectra in the main peak region. (***B***, ***D***) The normalised emission intensity is plotted against the UV exposure time, and fitted with an exponential approach.

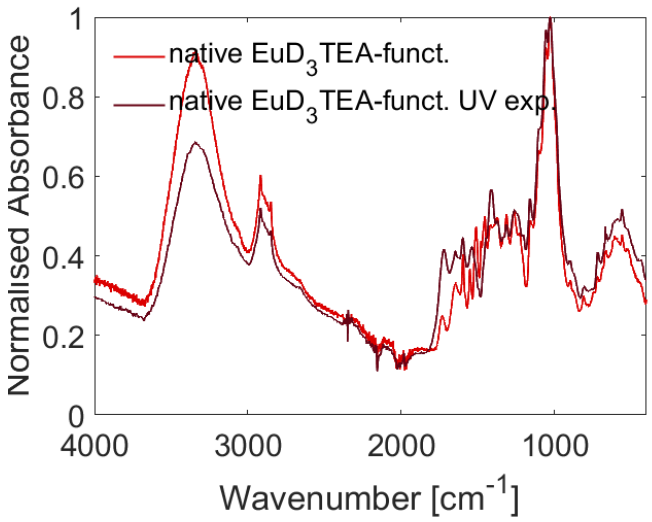

Figure S11. ATR-FTIR spectra of EuD_3TEA-functionalised native wood before and after 5 h of photostability analysis.

Comparison with Fluorescein

Fluorescein, an organic fluorophore with pH-responsive fluorescence, was used as a reference. A 1 mM fluorescein solution was prepared by dissolving the powder in MilliQ water and adjusting the pH to 8 with 1 M NaOH. [2]

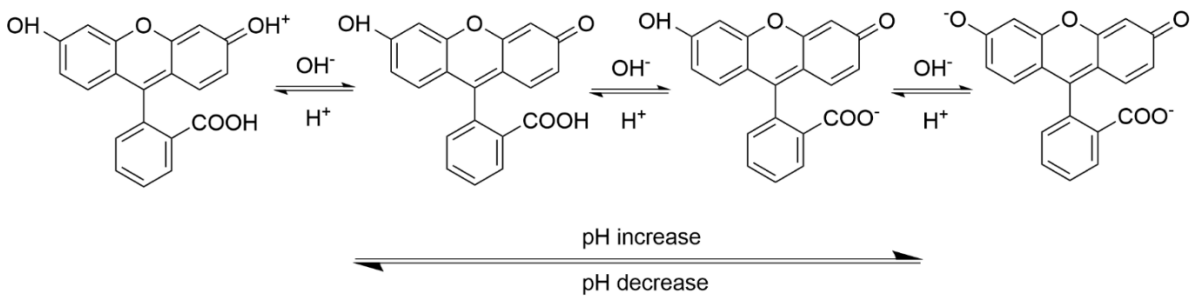

Figure S12. pH-Dependent behavior of fluorescein [2].

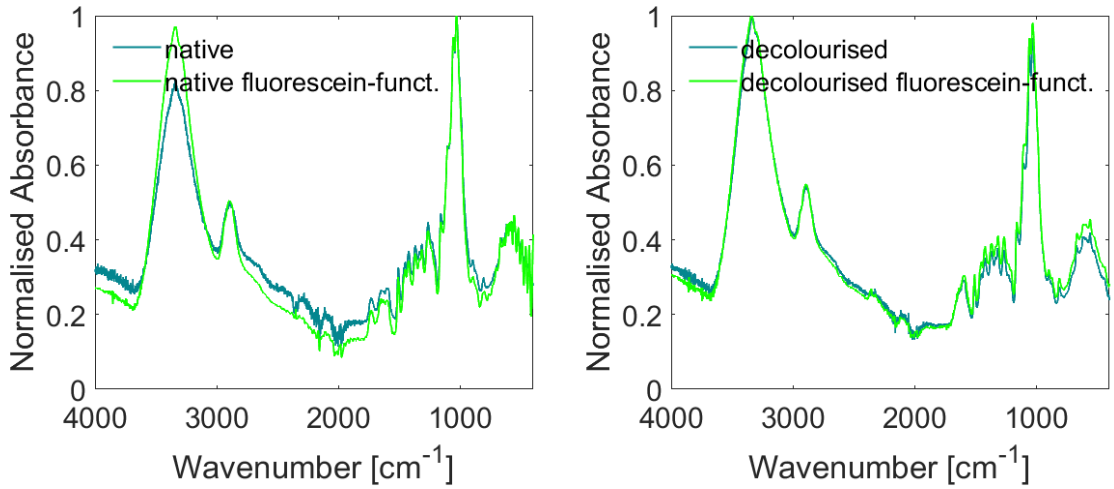

Figure S13. ATR FTIR spectra of (***A***) native spruce and fluorescein-functionalised native spruce, (***B***) decolourised and fluorescein-functionalised decolourised spruce.

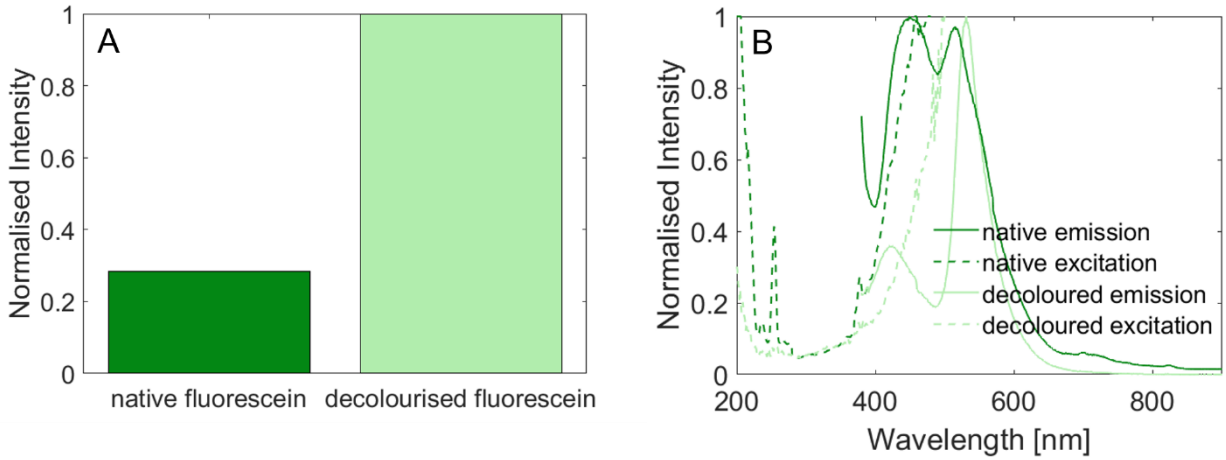

Figure S14. (***A***) Luminescence shine-through intensity values (λ_{ex} = 375 nm) of fluorescein-functionalised native (*bright green bar*) and decolourised (*faint green bar*) spruce cross-sections. (***B***) Fluorescence emission (*full line*, λ_{ex} = 361 nm) and excitation (*dotted line*, λ_{em} = 515 nm) spectra of fluorescein-functionalised native (*dark green line*) and decolourised (*faint green line*) spruce samples. In contrast with what observed for EuD_3TEA, the position of fluorescein's emission maxima is different in native and decolourised wood. The reason for this behaviour is still unclear.

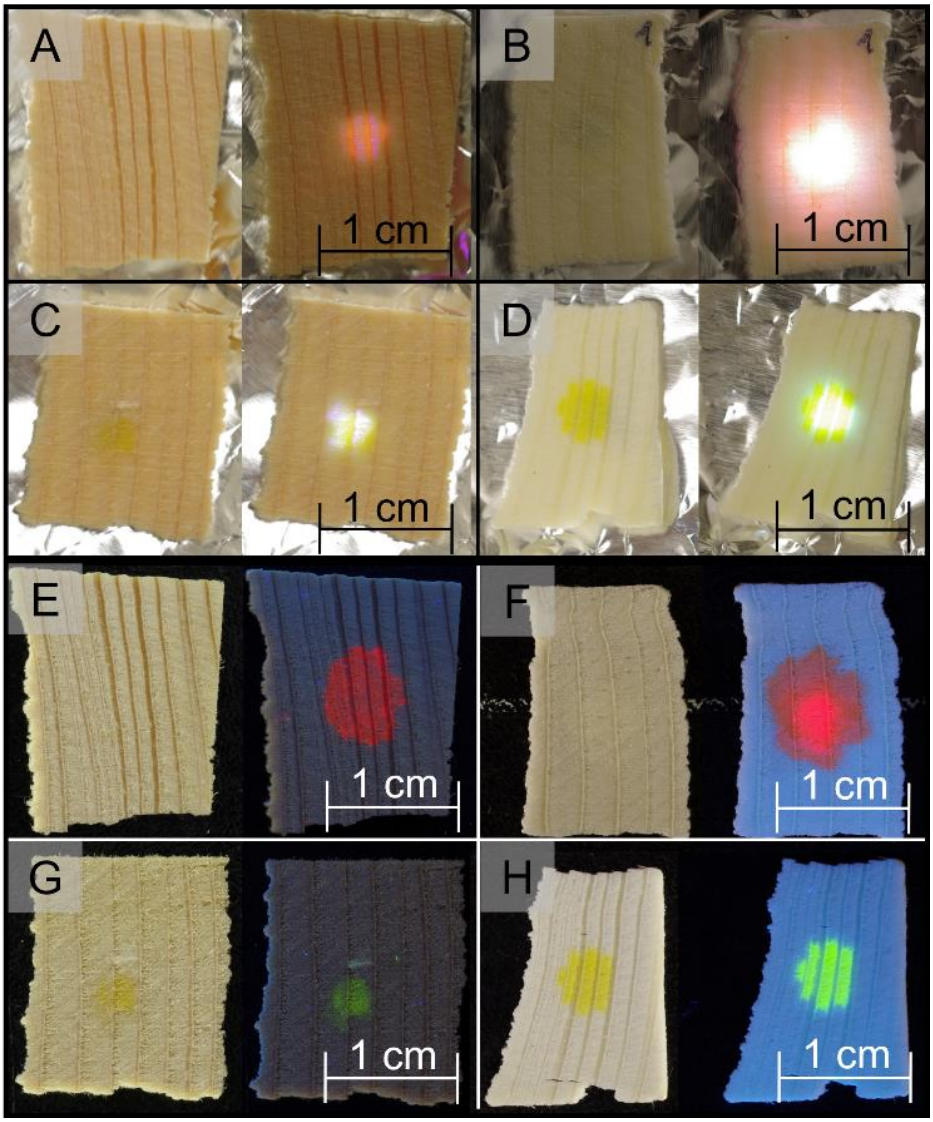

Figure S15. Comparison between EuD_3TEA- and fluorescein-functionalised native and decolourised spruce cross-sections illuminated from the bottom (**A**-**D**) and the top (**E**-**H**). In all cases, 10 µl of either a 10 mM (EuD_3TEA) or 1 mM (fluorescein) solution were deposited on the samples. Functionalisation with fluorescein leaves the wood with a strong yellow colour, while the EuD_3TEA functionalisation leaves the wood colour unaffected.

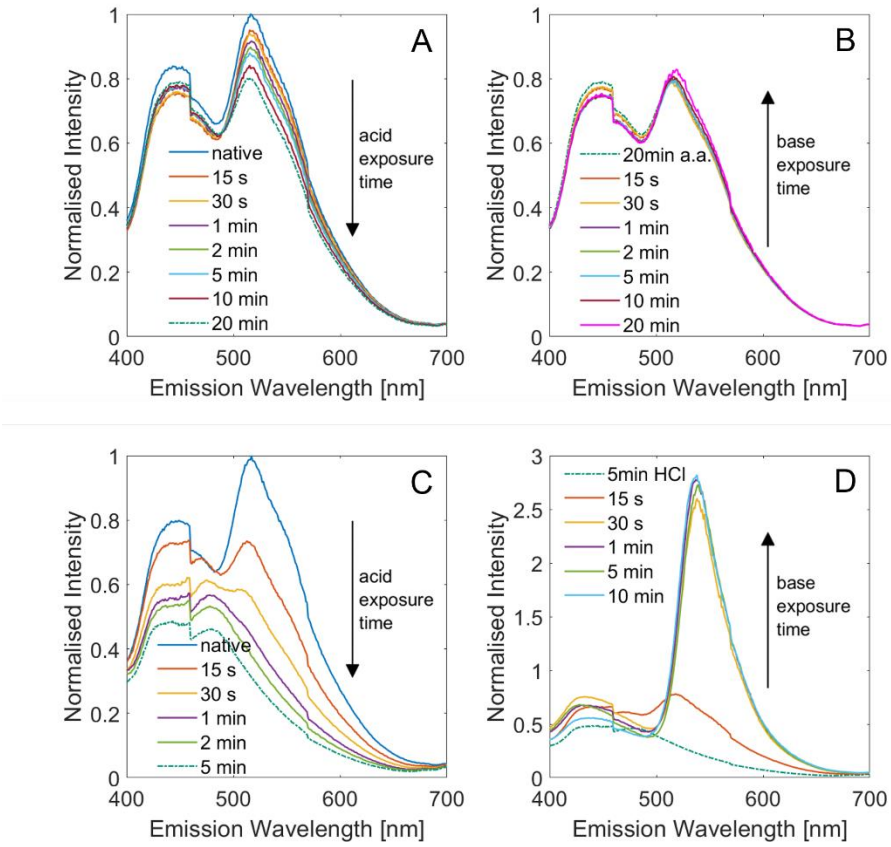

Figure S16. Fluorescence spectra of fluorescein-functionalised native wood cross-sections as a function of exposure to acidic ((***A***) acetic acid, (***C***) HCl) and alkaline vapours ((***B***) Et_3N, (***D***) NH_3). The results' interpretation is complicated by the partial overlap of fluorescein's main peak (~515 nm) on the shoulder of an additional peak (~430 nm, due to lignin's fluorescence) which also changes in response to vapour exposure. Notably, the emission of fluorescein is considerably enhanced by NH_3.

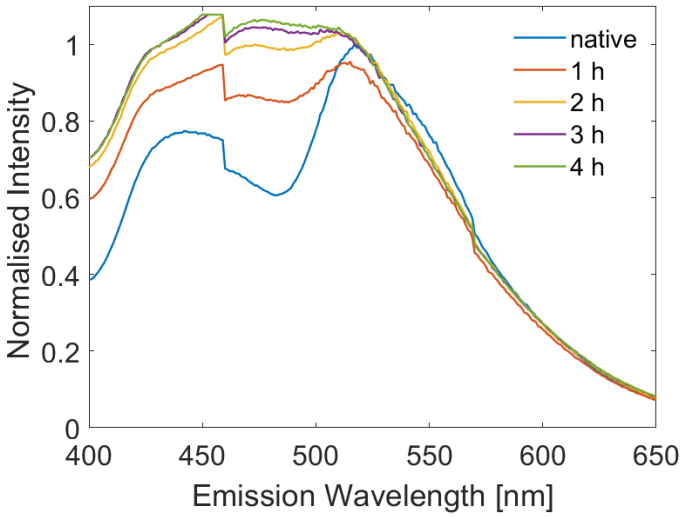

Figure S17. Photostability of fluorescein-functionalised native spruce. Normalised fluorescence intensity after different exposure times to a 1000 W m^{-2} UV light source (main emissions at ~400 nm and ~500 nm). The difficulty to analyse the fluorescence (**Figure S14**) holds also for the photostability results, as the lignin peak changes together with the fluorescein one.

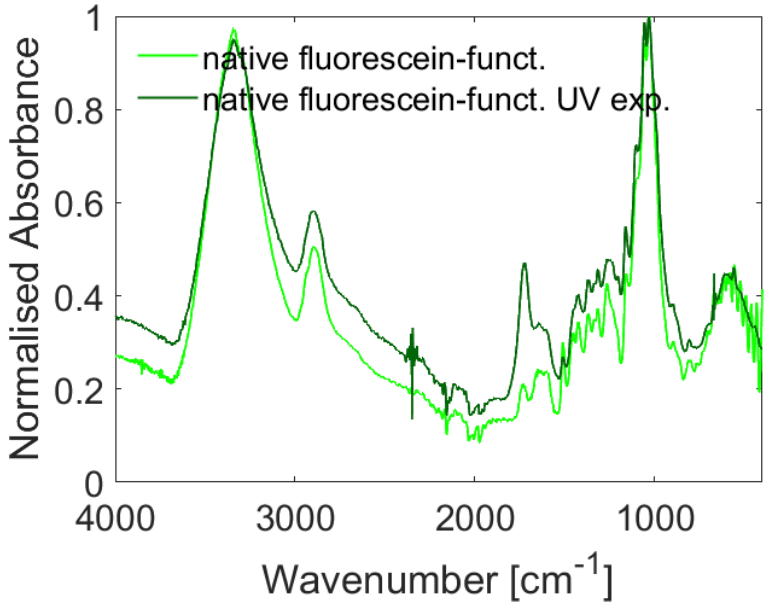

Figure S18. Comparison of the ATR-FTIR spectra of fluorescein-functionalised native wood before and 5 hours after the photostability test.

References

[1] R. S. Fontenot, K. N. Bhat, W. A. Hollerman, and M. D. Aggarwal, "Triboluminescent materials for smart sensors," *Mater. Today*, vol. 14, no. 6, pp. 292–293, 2011, doi: 10.1016/S1369-7021(11)70147-X.

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