Electronic Supplementary Information

Preparation of photochromic paper, using fibre-attached spiropyran polymer networks

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I. Materials and compounds

The following reagents and chemicals were used as received of the given purity from the corresponding suppliers:

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azobisisobutyronitrile (AIBN)</td>
<td>&gt;98 %</td>
<td>Fluka</td>
</tr>
<tr>
<td>4-Hydroxybenzophenone</td>
<td>98 %</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>3-Iodopropanoic acid</td>
<td>98 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>2,3,3-Trimethylindolenine</td>
<td>98 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>5-Nitrosalicylaldehyde</td>
<td>99 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>N-(3-Aminopropyl)methacrylamide hydrochloride</td>
<td>&gt;98 %</td>
<td>Polysciences Europe GmbH</td>
</tr>
<tr>
<td>N,N-Dimethylformamide (DMF)</td>
<td>99.5 %</td>
<td>Roth</td>
</tr>
<tr>
<td>1-Hydroxybenzotriazole monohydrate (HOBt*H$_2$O)</td>
<td>99.2 %</td>
<td>Iris Biotech</td>
</tr>
<tr>
<td>N-(3-Dimethylaminopropyl)-N$^\prime$-ethylcarbodiimide hydrochloride (EDC*HCl)</td>
<td>For synthesis</td>
<td>Nova Biotech</td>
</tr>
<tr>
<td>Sodium bicarbonate</td>
<td>99 %</td>
<td>Gruessing GmbH</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>99 %</td>
<td>Gruessing GmbH</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>99 %</td>
<td>Gruessing GmbH</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>99 %</td>
<td>Gruessing GmbH</td>
</tr>
<tr>
<td>Piperidine</td>
<td>98 %</td>
<td>Roth</td>
</tr>
<tr>
<td>Methyl ethyl ketone (MEK)</td>
<td>99.8 %</td>
<td>Sasol Solvents</td>
</tr>
<tr>
<td>Methanol</td>
<td>&gt;99.5 %</td>
<td>BASF</td>
</tr>
<tr>
<td>Chloroform</td>
<td>p.a.</td>
<td>Brenntag</td>
</tr>
<tr>
<td>Acetone</td>
<td>&gt;99.5 %</td>
<td>Roth</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>&gt;99.5 %</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>

$N,N$-Dimethylacrylamide (DMAA, 99 %, Sigma Aldrich) and methacryloyl chloride (97 %, Sigma Aldrich) were flushed through a basic alumina column followed by distillation under reduced pressure and stored under nitrogen atmosphere prior to use. 4-Methacryloxybenzophenone (MABP) was synthesized according to the literature.\textsuperscript{1} 1’-(2-(Propylcarbamylmethacrylamide)ethyl)-3’,3’-dimethyl-6-nitrospiro[2H-1]benzopyran-2,2’-indoline (NSp monomer) was synthesized according to literatures.\textsuperscript{2,4}

Commercially available Roth Rotilabo$^\circledast$ 15A filter paper (grammage: 84 g m$^{-2}$, BET area: 1.2 m$^2$ g$^{-1}$, mean pore diameter: 4.6 $\mu$m) was used as model substrate.
II. Instruments

$^1$H-NMR spectra were recorded in DMSO-$d_6$ or CDCl$_3$ on a Bruker DRX300 (300 MHz) instrument at 25 °C. Data were analyzed by software (MestreNova, Mestrelab Research S.L.).

Size exclusion chromatography (SEC) measurement was performed in a Hewlett-Packard Agilent 1200 series instrument equipped with two columns (PSS Gram VS 3a and PSS Gram VS 3b) in series with the eluent of 3 g L$^{-1}$ of LiCl in DMF at 30 °C. The system was calibrated using narrow-dispersed poly(methyl methacrylate) standards (PSS, Germany).

FTIR spectra were recorded on a PerkinElmer Spectrum One FTIR spectrometer equipped with a PerkinElmer SINGLE reflection UATR unit. 10 scans were accumulated with a resolution of 4 cm$^{-1}$. Each sample was measured by 5 times.

SEM photomicrographs were captured using a JEOL JSM-6510 scanning electron microscope operated at an acceleration voltage of 15 kV.

Elemental analysis was performed on an Elemental Analysis system (Vario EL III CHN).

Color digitalization was performed by means of a commercially available scanner (Canon Scan LiDE 200 with a resolution of 1200 dpi). Color analysis was carried out by ImageJ (1.46r, Wayne Rasband, National Institutes of Health, USA). The applied scientific camera (as a reference) is Canon PowerShot SX220 HS.

Thickness of lab-engineered paper sheets was measured by a digital caliper (PRECISE PS 7230).

UV transmittance was measured by Radiometer Photometer (ILT 1400-A, International Light Technologies).

For UV illumination, a VilberLourmat Bio-Link BLX UV exposure chamber ($\lambda = 365$ nm or 254 nm) was used. Each illumination experiment was performed by at least three times.

For Visible light illumination, a Lumatec Superlite SUV-DC light source (200 W super pressure short mercury lamp) equipped with liquid fiber optics ($\Phi = 0.5$ cm) and a filter with light in the visible light range ($\lambda = 400$ to 700 nm) was used.
III. Experimental procedures

Synthesis of P(DMAA-co-MABP-co-NSp):\(^4\)

![Scheme S1](image.png)

Scheme. S1 Schematic illustration of the radical copolymerization to yield spiropyran-functional terpolymers used to chemically modify the surface of paper fibers.

\(^{N,N}\)-Dimethylacrylamide (DMAA, 12 mL, 116.5 mmol), 4-methacryloxybenzophenone (MABP, 332.8 mg, 1.3 mmol, 1 mol%), and 1'-{(2-((propylcarbamyl)methacrylamide)ethyl)-3’,3’-dimethyl-6-nitrospiro[2H-1]benzo[pyran-2,2’]-indoline (NSp, 3.15 g, 6.25 mmol, 5 mol%) were added to chloroform (50 mL) in a Schlenk flask under nitrogen atmosphere followed by the addition of initiator (AIBN, 62.6 mg, 0.4 mmol, 0.3 mol%). The solution was degassed by three freeze-pump-thaw cycles. Subsequently, the mixture was stirred at 70 °C for 10 h. After that time, the solvent was evaporated, the gel-like solid was re-dissolved in acetone (70 mL) and the polymer was precipitated in diethyl ether (Et\(_2\)O, 700 mL). The crude product was purified by re-precipitation from acetone to diethyl ether for three times. After drying in vacuo, the polymer was yielded as a slightly purple solid (8.43 g, 56 %). The resulting polymer was characterized by \(^1\)H-NMR spectroscopy and size exclusion chromatography (SEC) for the quantification of their molar composition and molar mass, respectively. According to Fig. S1, the signal at 2.88 ppm is attributed to the two methyl groups (6\(\times\)) from the DMAA moieties, the signal at 5.84 ppm is attributed to one vinyl proton (1\(\times\)) from NSp moieties, and the signals between 7.40 and 7.90 ppm are attributed to the aromatic protons (7\(\times\)) from the MABP units. The molar composition of the resulting terpolymer was quantified according to their corresponding integral intensities. After calculation, approximately 2 mol\% of MABP and 5 mol\% of NSp were present in the terpolymer, named as P(DMAA\(_{93}\)-co-MABP\(_2\)-co-NSp\(_5\)). The SEC results (Fig. S2) show the number average molar mass (M\(_n\)) and the weight average molar mass (M\(_w\)) of the polymer are 35.000 and 104.000 g mol\(^{-1}\), respectively. The calculated dispersity (M\(_w\)/M\(_n\)) is 2.92.
**Fig. S1** $^1$H-NMR spectrum of P(DMAA$_{93}$-co-MABP$_2$-co-NSp$_5$) measured in CDCl$_3$.

**Fig. S2** SEC chromatogram of P(DMAA$_{93}$-co-MABP$_2$-co-NSp$_5$).
Synthesis of $\text{P(DMAA-co-MABP)}$:\(^4\)

\[
\text{Acrylonitrile} + \text{MABP}
\xrightarrow{\text{AIBN, 70 °C, CHCl}_3}
\text{copolymer}
\]

**Scheme. S2** Schematic illustration of the radical copolymerization to yield a copolymer that is used as reference material.

DMAA (12.5 mL, 121.3 mmol) and MABP (660.5 mg, 2.5 mmol, 2 mol%) were dissolved in chloroform (50 mL) under nitrogen atmosphere followed by the addition of initiator AIBN (62.6 mg, 0.4 mmol, 0.3 %). The solution was degassed by three freeze-pump-thaw cycles. Subsequently, the mixture was stirred at 70 °C for 1 h. After that time, the solvent was evaporated, the gel-like solid was re-dissolved in acetone (100 mL) and precipitated in diethyl ether ($\text{Et}_2\text{O}$, 1000 mL). The polymer was purified by reprecipitation from acetone to diethyl ether for three times. After drying in vacuo, the polymer was yielded as a colorless solid (9.38 g, 74 %). The resulting polymer was characterized in the same manner as above. Approximately 2 mol% of MABP were present in the copolymer, named as $\text{P(DMAA}_{98}\text{-co-MABP})$. The number average molar mass ($M_n$) and the weight average molar mass ($M_w$) of the copolymer are 62.000 and 211.000 g mol\(^{-1}\), respectively. The calculated dispersity was 3.43.

**Preparation of lab-engineered paper sheets:**

The preparation of lab-engineered paper sheets was carried-out according to a recently published protocol.\(^5\) In brief, dry cotton linters-fibers were refined in a Voith LR 40 laboratory refiner with an effective specific energy of 200 kWh t\(^{-1}\). A series of paper sheets having different grammages (23, 32, 55, 79, 120 g m\(^{-2}\)) and various thicknesses of isotropically layered cellulose fibers were processed on a conventional Rapid-Koethen hand sheet maker according to DIN 54358 and ISO 5269/2 without any additives and fillers. After preparation, all paper sheet samples were stored in a climate room (norm climate: 23 °C, 50 % relative humidity) prior to further use. The thickness and UV transmittance of self-made paper sheets are shown in **Table 1**.
Table 1 Grammage, thickness and UV transmittance of lab-engineered cotton linters sheets prepared by Rapid Koethen process.

<table>
<thead>
<tr>
<th>Grammage/g m⁻²</th>
<th>Thickness/µm</th>
<th>UV transmittance/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 ± 0.5</td>
<td>58 ± 2</td>
<td>40.1 ± 0.7</td>
</tr>
<tr>
<td>32 ± 0.8</td>
<td>77 ± 2</td>
<td>31.7 ± 1.0</td>
</tr>
<tr>
<td>55 ± 0.8</td>
<td>112 ± 1</td>
<td>20.5 ± 0.5</td>
</tr>
<tr>
<td>79 ± 0.7</td>
<td>151 ± 3</td>
<td>14.9 ± 0.2</td>
</tr>
<tr>
<td>120 ± 0.5</td>
<td>211 ± 2</td>
<td>8.5 ± 0.1</td>
</tr>
</tbody>
</table>

Preparation of polymer-modified paper sheets:

For the modification of paper substrates (Roth 15A, 1 × 1 cm²), the reference polymer (P(DMAA₉₈-co-MABP₂)) or the spiropyran-functionalised polymer (P(DMAA₉₃-co-MABP₂-co-NSp₅)) were first dissolved in THF at a concentration of approximately 30 mg mL⁻¹. After immersed into the polymer solution for 20 s, the paper substrates were pulled out at a constant velocity of 1 cm min⁻¹ followed by air drying for at least 30 min in the dark. The paper sheets were then illuminated by UV light (λ = 254 nm) in a VilberLourmat Bio-Link BLX UV exposure chamber with the energy of 400 mJ cm⁻². Note, approximately 94% of the benzophenone groups had been excited which ensures a firm crosslinking of the polymer to the fiber surface. Finally, non-bound polymer was removed from the paper substrate by Soxhlet extraction (THF, 150 min) and the sheets were air-dried overnight in the dark. All so-prepared samples were stored in the dark under norm-climate conditions prior to further investigation.

Investigation of the switching behavior of spiropyran-functionalised paper:

For light switching, different UV (or Vis) doses were applied to the (modified) paper substrate. According to the manufacturer’s data, the flux density of the visible light is approximately 40 mW cm⁻² at a distance of 8 cm from the tip of the fiber optics. After illumination, a digital image of the sample was taken using an office scanner and the image color was analyzed by software (ImageJ).
IV. Dynamic sensitivity adjustment by a damping method

The sensitivity of the photo-responsive material can be dynamically adjusted by the control of the photons reaching the spiropyran-modified surface. The spiropyran-modified paper was covered with another unmodified paper as a damping material. The damping paper was attached using metal masks on the edges to ensure a tight contact between both paper sheets and to define the illumination zone (Scheme S3).

Scheme S3 Schematic illustration of damping setup using unmodified paper.

To describe the transmission of light in case of our paper system, we used a simple Beer-Lambert law ansatz. In this case, we treat paper as a light absorbing medium. We know that this may only be a rough estimate, accounting for the scattered light not being collected in the detector. The schematic illustration for this is shown in Scheme S4.
Scheme S4 Schematic illustration of light passes through paper according to Beer-Lambert law.

The general Beer-Lambert law is defined as follows:

\[ A = \log \left( \frac{I}{I_0} \right) = \log \left( \frac{I}{I_0} \right) = \varepsilon \cdot c \cdot z \]

where \( A \) = absorbance, \( T \) = transmission, \( I_0 \) = light intensity before passing through the medium, \( I \) = light intensity of transmitted light, \( \varepsilon \) = extinction coefficient, \( c \) = concentration of the absorbing species, \( d \) = distance that the light has to travel through the sample.

In the case of our paper system, \( z \) corresponds to the thickness of the damping paper. According to the work of Whitesides, we replaced \( \varepsilon \cdot c \) by a paper specific coefficient \( \alpha_{\text{samp}} \) to describe the light properties of cellulosic fibers.\(^6\) Furthermore, the authors introduced a variable \( (T_c) \) for describing the characteristic transmittance of paper. Consequently, absorbance \( (A) \) can be described as

\[ A = \alpha_{\text{samp}} \cdot z \]

and transmittance \( (T) \) as

\[ T = 10^{-A} = T_c \cdot 10^{-\alpha_{\text{samp}} \cdot z} \]

Herein, “absorbance” may be similarly treated as light that is “lost” by the light scattering of cellulosic fibers. The UV transmittance of damping paper sheets exponentially decreases as the grammage, the thickness or the density of paper sheets increases (Fig. S3 b, d and f). The UV absorbance of damping paper sheets linearly increases as the grammage, the thickness or the density of paper sheets increases (Fig. S3 a, c and e). Note, although \( \alpha_{\text{samp}} \) has a physical meaning, in our case we did not intend to study this in further detail, as the provided model can only be a rough estimate. Nevertheless, it is interesting to observe that the general relations being expressed in the equations above were found in the experimental data (shown in Fig. S3). The latter indicates a high level of reproducibility of the damping by applying sheets of varying grammage (i.e. fiber density as well as sheet thickness, respectively).
Fig. S3  

a) UV absorbance and b) transmittance of damping paper sheets as a function of paper thickness with a linear/exponential fit (the fitting equations shown as inset);  

c) UV absorbance and d) transmittance of damping paper sheets as a function of paper grammage with a linear/exponential fit (the fitting equations shown as inset);  

e) UV absorbance and f) transmittance of damping paper sheets as a function of paper density with a linear/exponential fit (the fitting equations shown as inset).
V. Analysis of photochromic paper

Fig. S4 SEM images of unmodified paper and spiropyran-functionalised paper: (a) top-view of unmodified paper; (b) top-view of spiropyran-functionalised paper; (c) cross-section of unmodified paper; and (d) cross-section of spiropyran-functionalised paper.

Fig. S5 UATR-FTIR spectra of unmodified paper (a), spiropyran-functionalised paper (b), and spiropyran polymer (c).
Fig. S6 Amount of immobilized spiropyran-containing polymer per gram of fiber as a function of the polymer concentration in the dip-coating solution (the dashed line is included to “guide the eye”).

Fig. S7 Grey values of the spiropyran-functionalised paper before UV illumination (the error bar is from software (ImageJ)).
**Fig. S8** Grey values of the spiropyran-functionalised paper after UV illumination with different UV dose from 0 to 2000 mJ cm$^{-2}$ (the error bar is from software (ImageJ)).

**Fig. S9** Images of spiropyran-functionalised paper before and after UV illumination by a UV dose of 1000 mJ cm$^{-2}$ obtained by an office scanner (a and c) and a scientific camera (b and d) with the grey value written below the images.
**Fig. S10** Scanned images of spiropyran-functionalised paper after UV illumination with different UV dose from 0 to 2000 mJ cm\(^{-2}\) under different damping conditions.

<table>
<thead>
<tr>
<th>Damping</th>
<th>Transmittance (%)</th>
<th>UV dose (mJ cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>u.a.</td>
<td>0, 30, 60, 90, 120, 150, 180, 210, 240, 250, 500, 750, 1000, 1250, 1500, 1750, 2000</td>
</tr>
<tr>
<td>Roth 15A one layer, 141 (\mu)m</td>
<td>11.41 ± 0.11</td>
<td></td>
</tr>
<tr>
<td>Roth 15A two layers, 272 (\mu)m</td>
<td>3.33 ± 0.03</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. S11** Grey value of UV-illuminated spiropyran-functionalised paper with a UV dose of 1000 mJ cm\(^{-2}\) as a function of storage time in the dark.
Fig. S12 (a) Scanned images of the spiropyran-functionalised paper after multiple switching cycles by alternating illumination by UV and visible light (a UV dose of 930 mJ cm$^{-2}$, a visible light dose of 36 J cm$^{-2}$); and (b) Normalized grey value of the spiropyran-functionalised paper by alternating illumination by UV and visible light as a function of switching cycles.

VI. References