

## Electronic Supplementary Information

### Boronate sol–gel method for one-step fabrication of polyvinyl alcohol hydrogel coatings by simple cast- and dip-coating techniques

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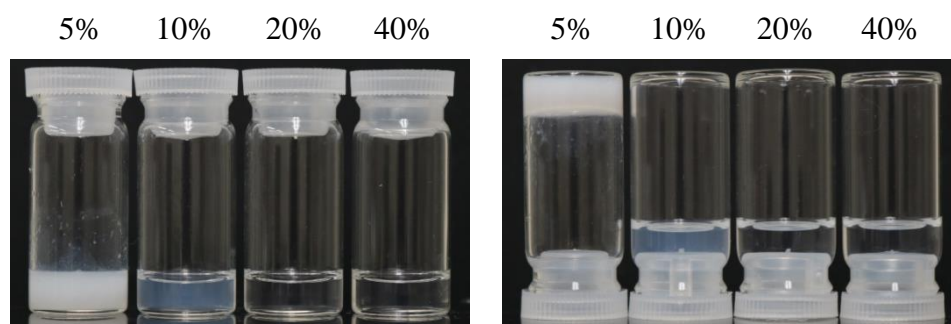
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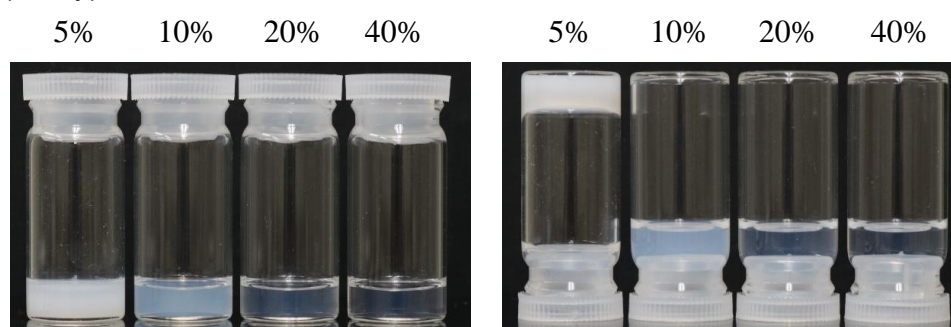
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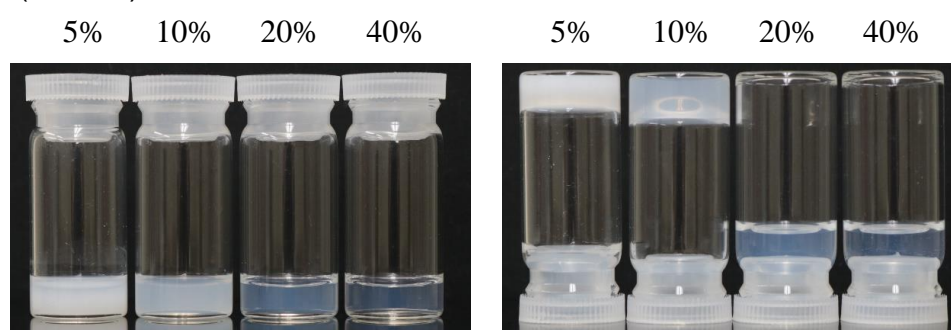
(a) 10 min



(b) 24 h (1 day)



(c) 168 h (1 week)



(d) 744 h (1 month)

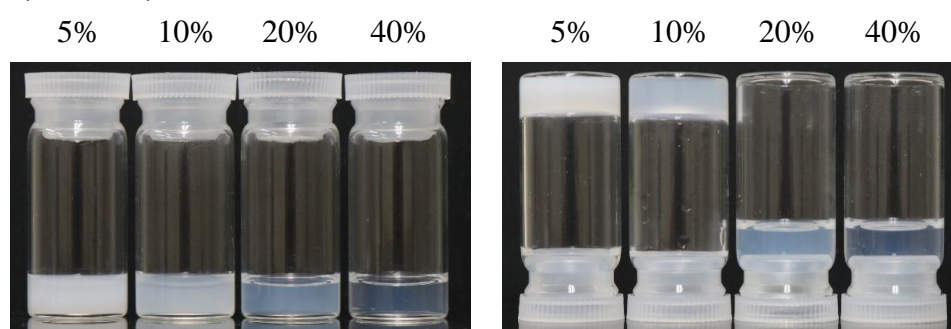


Fig. S1 Photographs of the mixtures of PVA and DBA in aqueous ethanol (1 mL) at different water fractions of 5% (v/v), 10% (v/v), 20% (v/v) and 40% (v/v) after standing for (a) 10 min, (b) 24 h, (c) 168 h and 744 h at room temperature. Photographs of samples placed upside down are also shown in the right side.

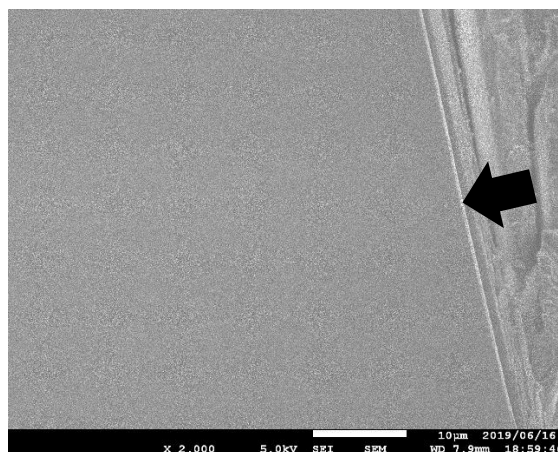
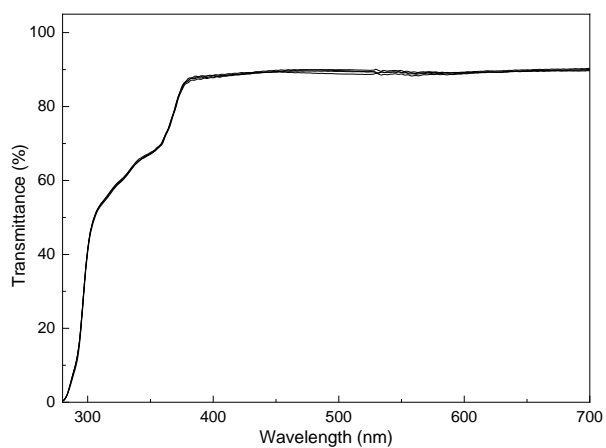


Fig. S2 FE-SEM image of the surface of a PVA/DBA film prepared on a polystyrene Petri dish. The right edge of the specimen is indicated by a black arrow.

(a)



(b)

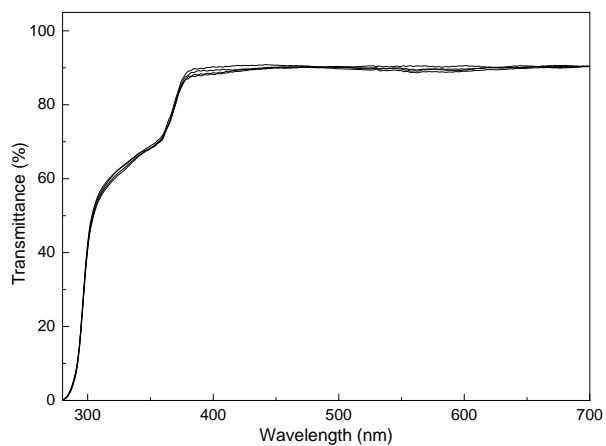


Fig. S3 UV-vis transmittance spectra of (a) uncoated polystyrene Petri dishes and (b) PVA/DBA-coated polystyrene Petri dishes.

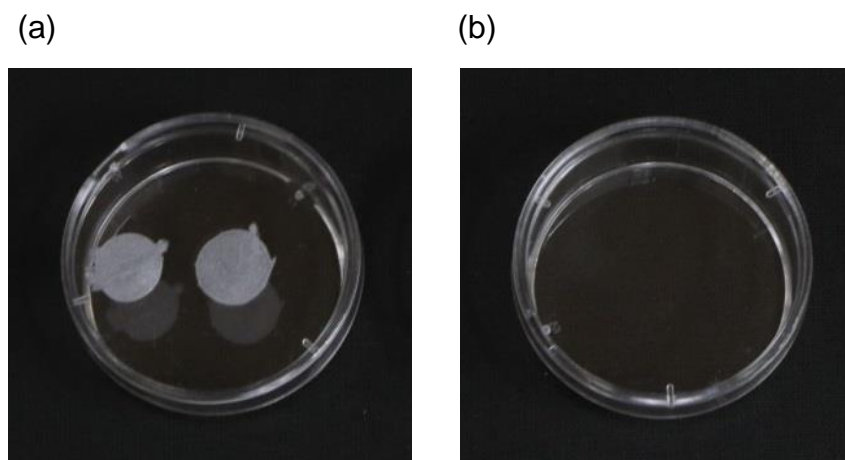


Fig. S4 Photographs of (a) an uncoated polystyrene Petri dish cover and (b) a PVA/DBA-coated polystyrene Petri dish cover after exposure to acetone. Two drops of acetone were put on the uncoated polystyrene Petri dish and the PVA/DBA-coated polystyrene Petri dish, respectively. The uncoated dish showed a fogging due to the partial dissolution of the petri dish in acetone. On the other hand, the PVA/DBA-coated dish showed negligible fogging due to the durability of the PVA/DBA film toward acetone.

Table S1. Characterization data of PVA/DBA coating films on polystyrene Petri dishes at different immersion periods in water.<sup>a</sup>

	Immersion time				
	As prepared	12 h	24 h	72 h	168 h
Weight (mg)	28.5 ± 1.4	28.3 ± 0.3	28.0 ± 1.5	28.4 ± 0.2	28.3 ± 0.6
Film thickness (mm)	3.0 ± 0.3	2.9 ± 0.6	3.6 ± 0.7	3.1 ± 0.4	3.0 ± 0.8
Optical transmittance at 660 nm (%)	90.2 ± 0.2	90.3 ± 0.2	90.5 ± 0.2	90.3 ± 0.5	90.2 ± 0.3
Contact angle of water droplet (°)	54 ± 2	51 ± 1	55 ± 4	53 ± 2	52 ± 5

<sup>a</sup> Four samples were individually analyzed for each immersion time.

Table S2. Stability of PVA/DBA coating films prepared from the mixtures of PVA and DBA in aqueous ethanol using aqueous solutions at different pH values. The obtained films on Petri dishes (9 cm in diameter) were immersed in water for 168 h (1 week).<sup>a</sup>

pH of aqueous solutions	Weight (mg)	
	Before immersion	After immersion
pH 5	25.0 ± 0.5	25.0 ± 0.7
pH 6	25.8 ± 0.4	25.8 ± 0.4
pH 7	25.6 ± 1.1	25.8 ± 0.8
pH 8	26.1 ± 0.4	26.4 ± 0.5
pH 9	26.1 ± 0.9	26.8 ± 0.6

<sup>a</sup>The pH values of aqueous solutions were adjusted using hydrochloric acid and aqueous sodium hydroxide. Four samples were individually prepared and characterized for each pH condition.

Table S3. The weights of PVA/DBA coating films on Petri dishes (9 cm in diameter) before and after immersion in aqueous solutions at different pH values for 168 h (1 week).<sup>a</sup>

pH of aqueous solutions	Weight (mg)	
	Before immersion	After immersion
pH 2 (0.01 M hydrochloric acid)	28.9 ± 0.5	28.5 ± 0.6
pH 3 (0.05 M glycine-HCl buffer)	28.9 ± 0.4	28.7 ± 0.5
pH 4 (0.1 M acetic acid-sodium acetate buffer)	27.5 ± 0.7	27.3 ± 0.4
pH 5 (0.1 M acetic acid-sodium acetate buffer)	28.6 ± 0.4	28.2 ± 0.5
pH 6 (0.1 M phosphate buffer)	27.4 ± 0.7	27.3 ± 0.6
pH 7 (0.1 M phosphate buffer)	28.6 ± 0.3	28.5 ± 0.4
pH 8 (0.1 M phosphate buffer)	27.5 ± 0.6	27.6 ± 0.5
pH 9 (0.1 M carbonate-bicarbonate buffer)	28.5 ± 0.3	25.0 ± 0.2
pH 10 (0.1 M carbonate-bicarbonate buffer)	28.9 ± 0.2	23.7 ± 0.5

<sup>a</sup>Four samples were individually prepared and characterized for each pH condition.

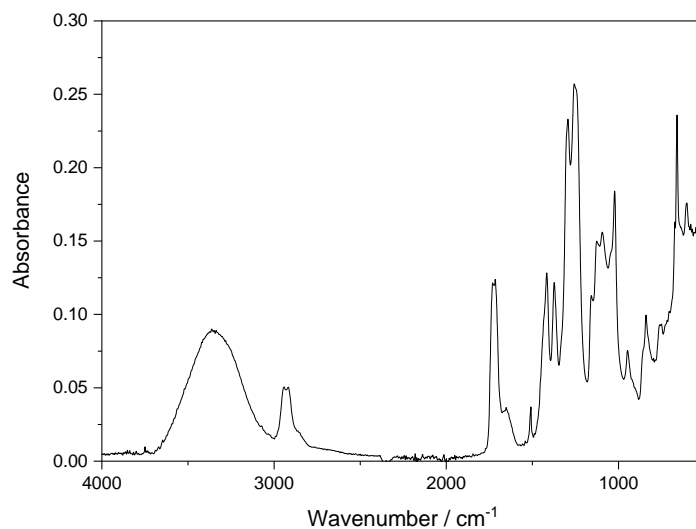


Fig. S5 ATR-FT-IR spectrum of a PVA/DBA film prepared on a polystyrene Petri dish.

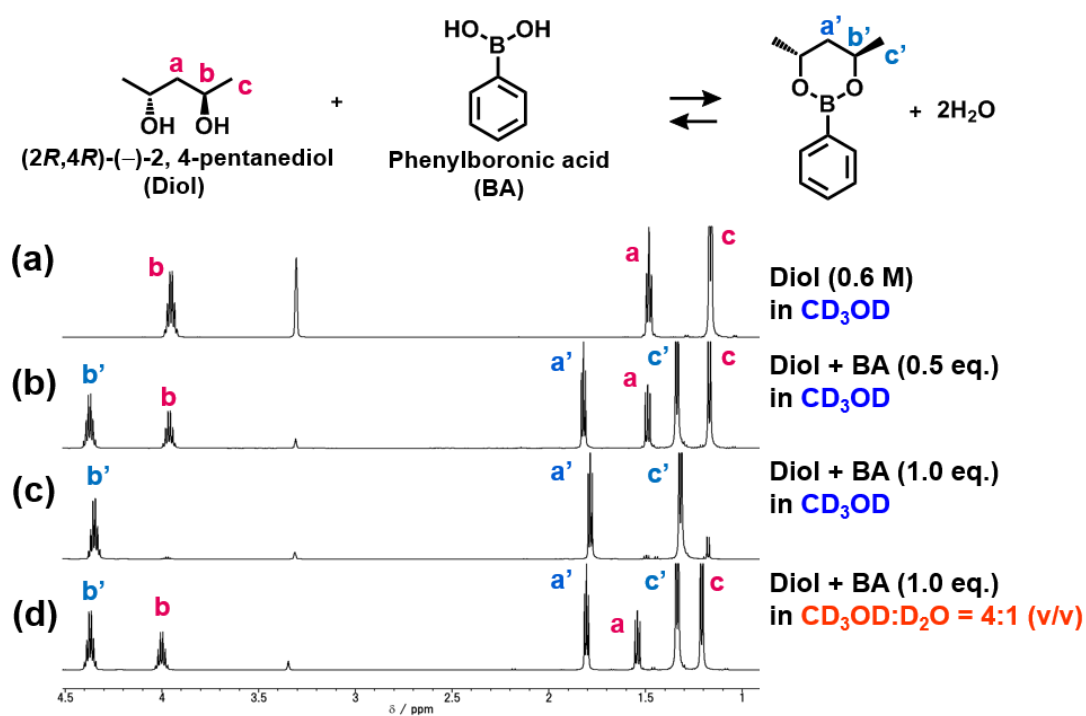


Fig. S6  $^1\text{H}$ -NMR spectra of (a) (2*R*,4*R*)-(-)-2,4-pentanediol (Diol, 0.6 M) in methanol- $d_4$ , (b) Diol and phenylboronic acid (BA, 0.3 M) in methanol- $d_4$ , (c) Diol (0.6 M) and BA (0.6 M) in methanol- $d_4$ , and (d) Diol (0.6 M) and BA (0.6 M) in methanol- $d_4/\text{D}_2\text{O}$  (4:1(v/v)).

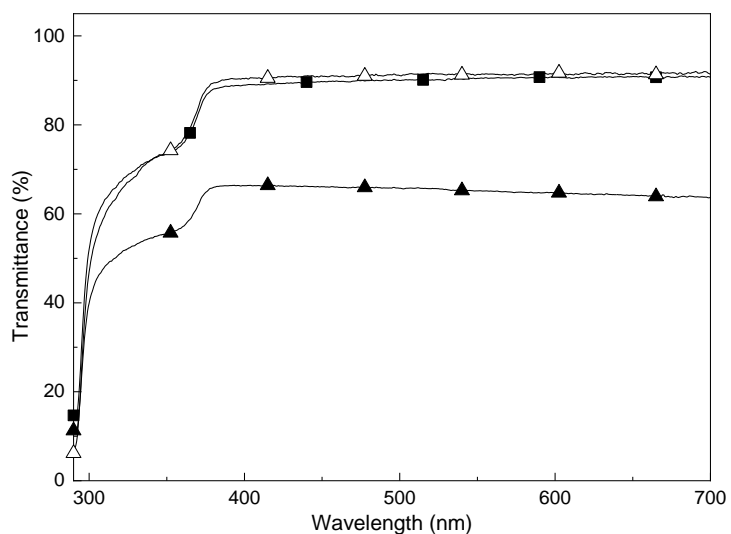


Fig. S7 UV-vis transmittance spectra of an uncoated polystyrene Petri dish (filled triangle) and a PVA/DBA-coated polystyrene Petri dish (open triangle) after exposure to water vapor from warm water (2 mL, 40 °C) and a UV-vis transmittance spectrum of a polystyrene Petri dish after exposure to water vapor (filled square).

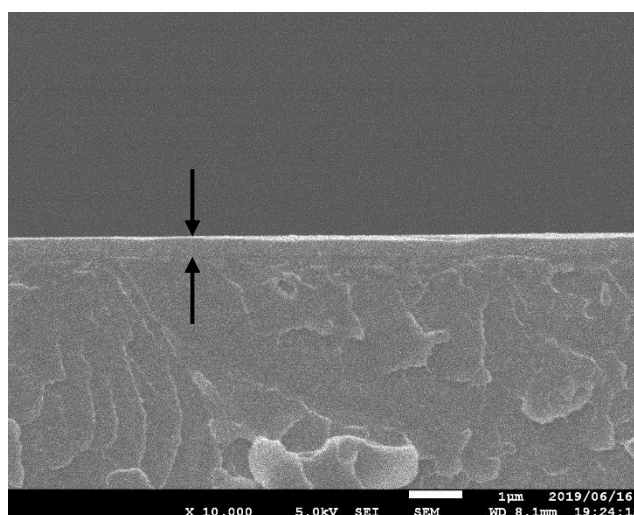
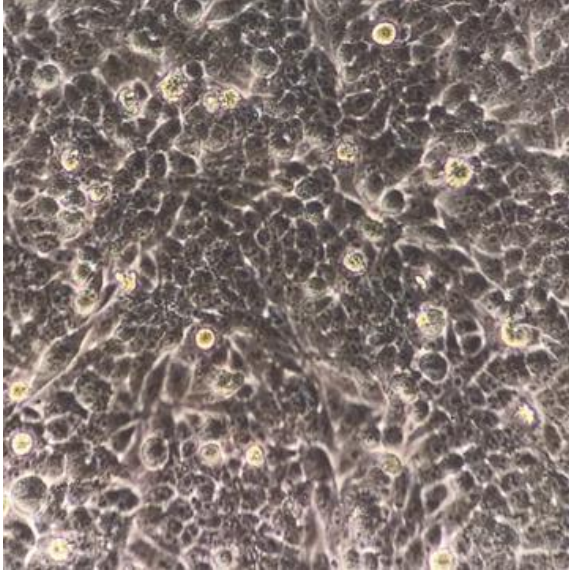


Fig. S8 FE-SEM image of the cross section of a PVA/DBA coating film on a 24-well culture plate prepared by a cast-coating method.



(a)



(b)

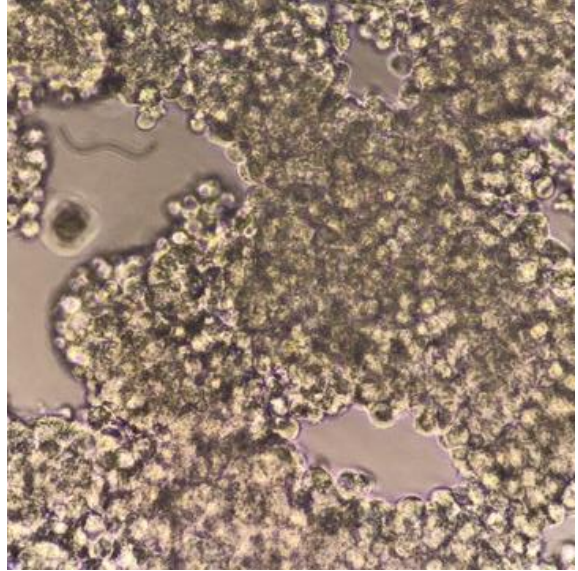
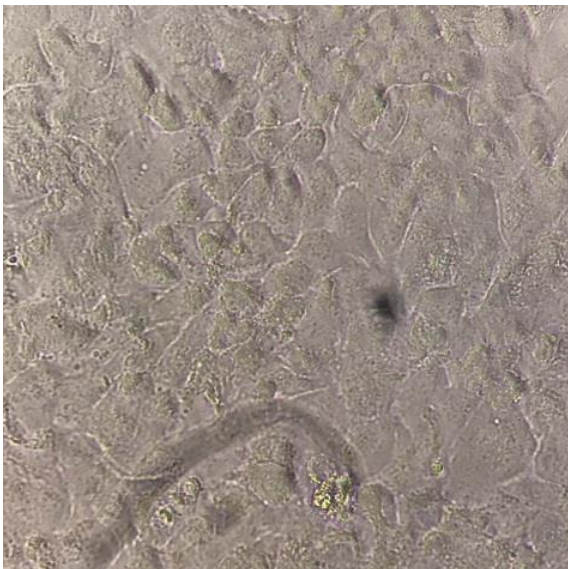


Fig. S9 Photographs of HeLa cells cultured for 24 h using (a) an uncoated 24-well PS tissue culture plate and (b) a PVA/DBA-coated 24-well PS tissue culture plate.

(a)



(b)



Fig. S10 Photographs of (a) an uncoated 24-well PS tissue culture plate and (b) a PVA/DBA-coated 24-well PS tissue culture plate after replacing the culture solutions of HaCaT skin keratinocytes with fresh culture media.

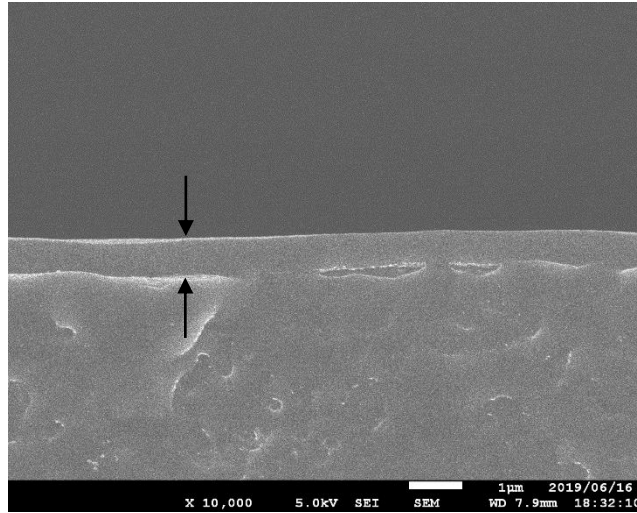


Fig. S11 FE-SEM image of the cross section of a PVA/DBA coating film on a polyethylene (PE) plate prepared by a dip-coating method.

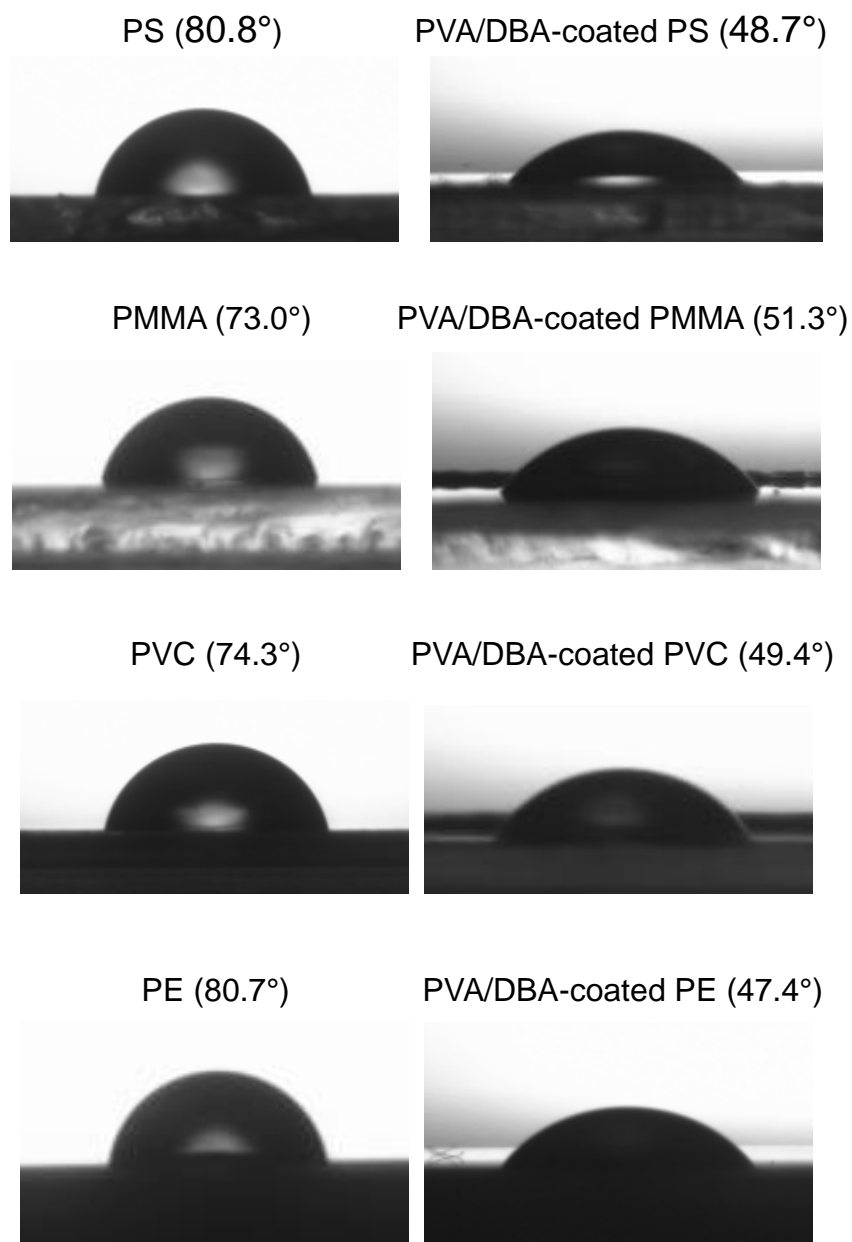


Fig. S12 Photographs and contact angles of water droplets on uncoated (left) and PVA/DBA-coated (right) plates (50 mm × 10 mm × 1 mm) of polystyrene (PS), polymethyl methacrylate (PMMA), polyvinyl chloride (PVC) and polyethylene (PE).

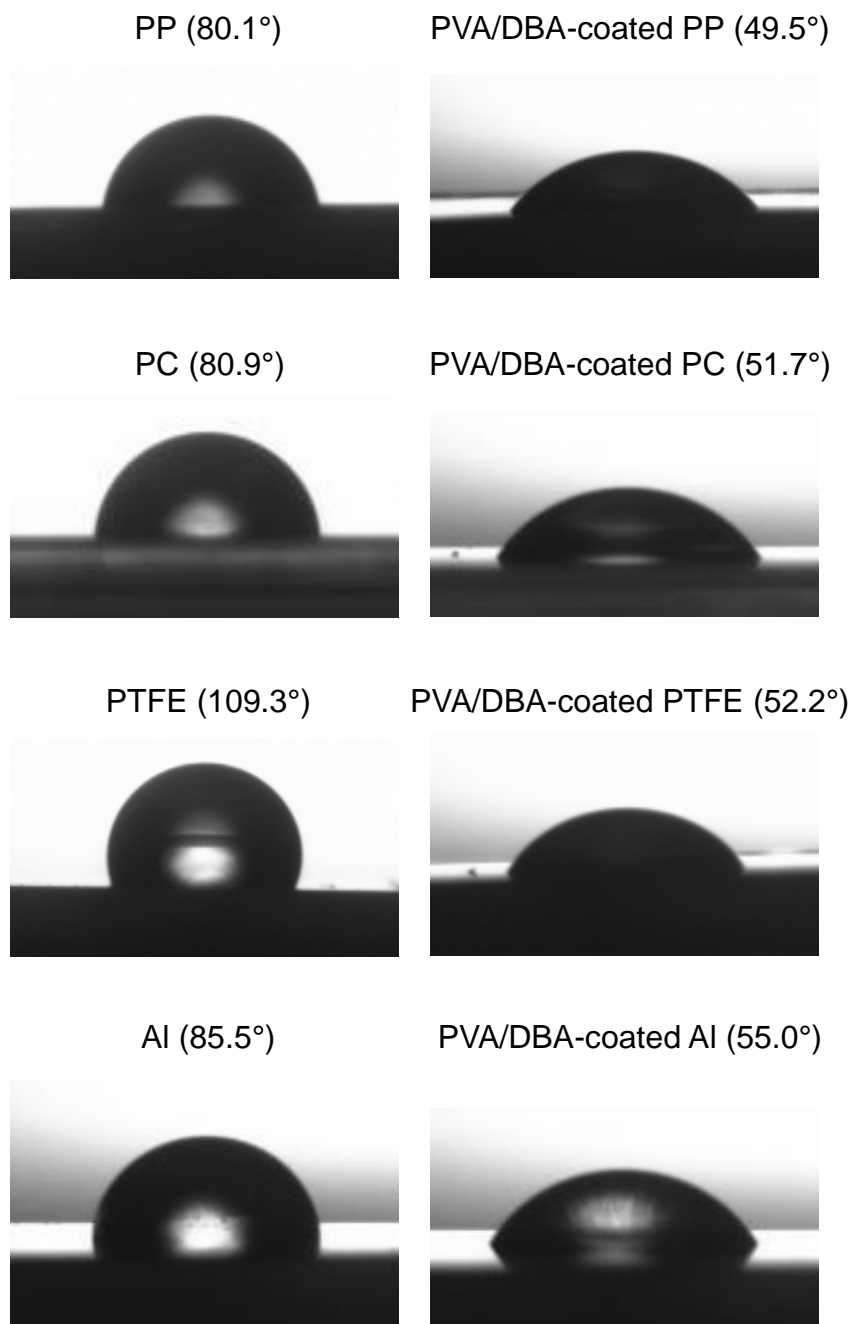


Fig. S13 Photographs and contact angles water droplets on uncoated (left) and PVA/DBA-coated (right) plates (50 mm × 10 mm × 1 mm) of polypropylene (PP), polycarbonate (PC), polytetrafluoroethylene (PTFE) and aluminum (Al).

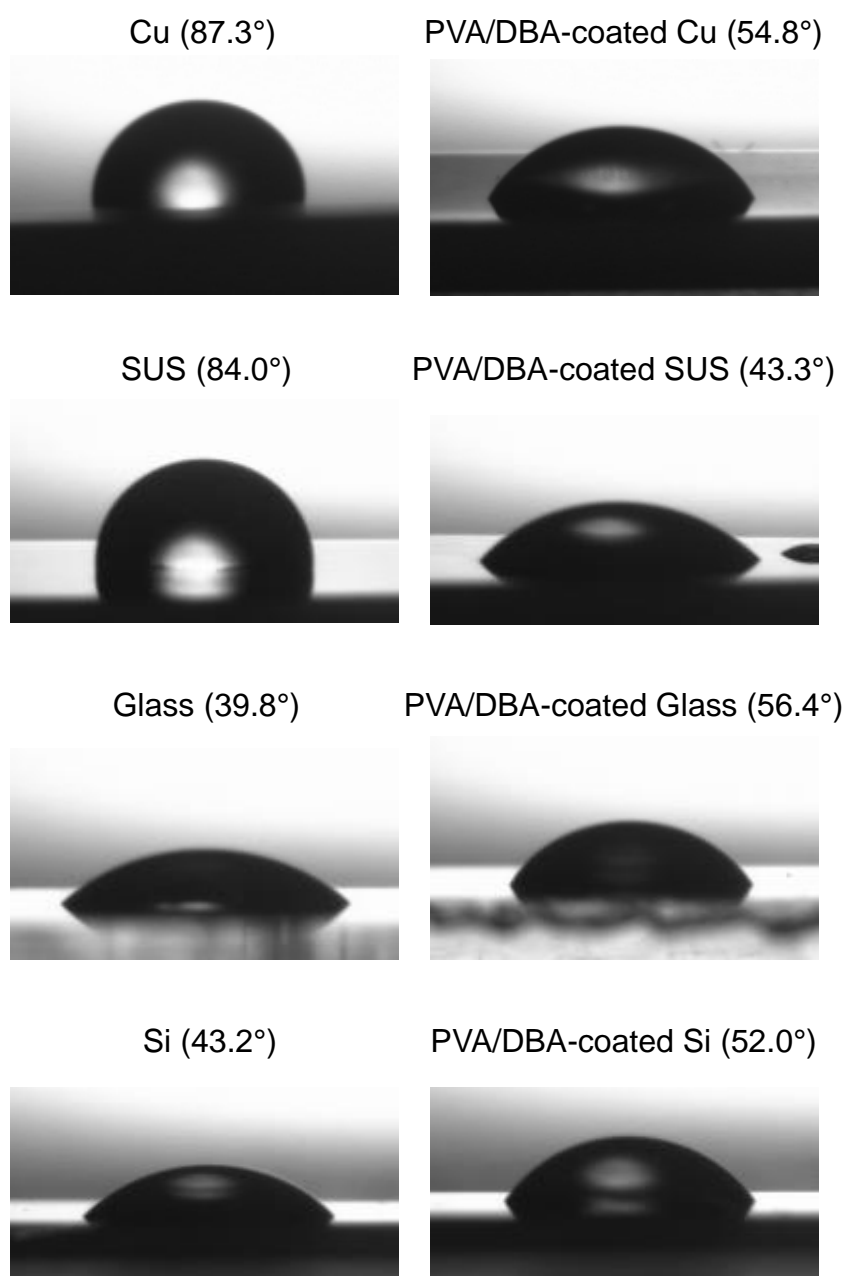


Fig. S14 Photographs and contact angles of water droplets on uncoated (left) and PVA/DBA-coated (right) plates (50 mm × 10 mm × 1 mm) of copper (Cu), stainless steel (SUS), glass (Glass) and silicon (Si).

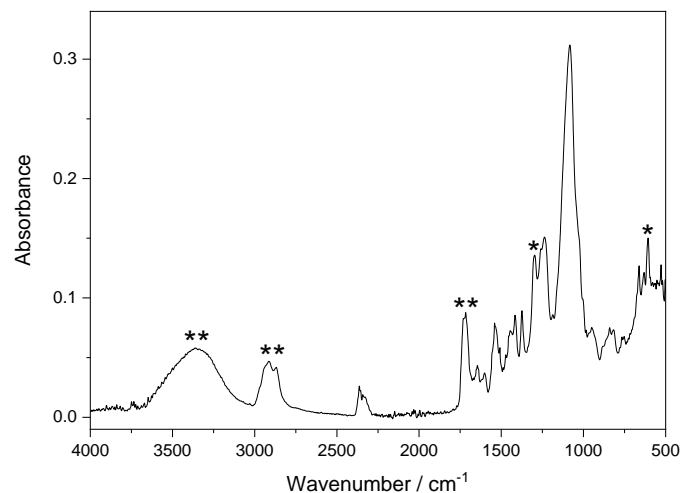


Fig. S15 ATR-FT-IR spectrum of a PVA/DBA-coated polyurethane sponge. Peaks marked with asterisks and double asterisks are assignable to the boronate esters (B-O stretching) and PVA (C=O, C-H and O-H stretching), respectively.

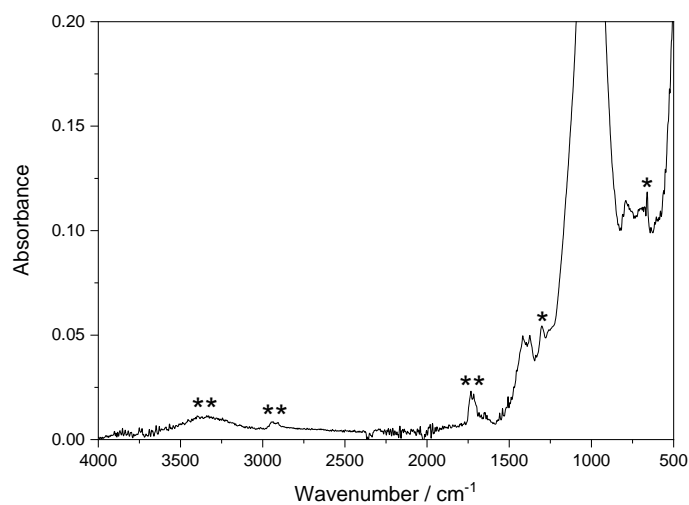


Fig. S16 ATR-FT-IR spectrum of a PVA/DBA-coated glass fiber filter paper. Peaks marked with asterisks and double asterisks are assignable to the boronate esters (B-O stretching) and PVA (C=O, C-H and O-H stretching), respectively.

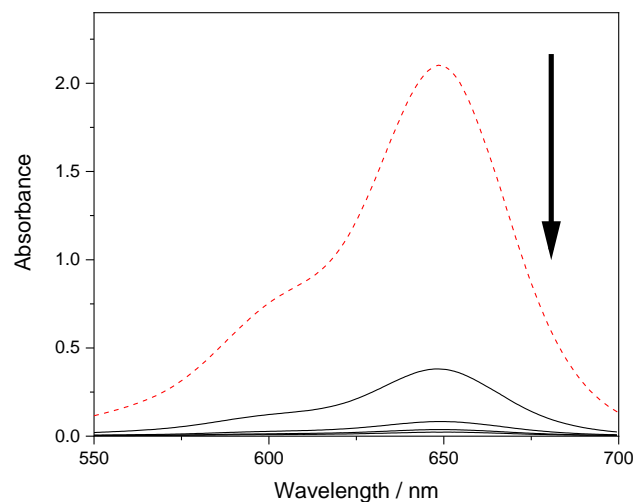


Fig. S17 UV-vis spectra of an erio green B (EG)-doped PVA/DBA film on a polystyrene Petri dish before (broken line) and after immersion in water (solid lines, immersion time: 5, 20, 60 and 120 min). A PVA/DBA-coated PS Petri dish was used as a reference for the measurements.

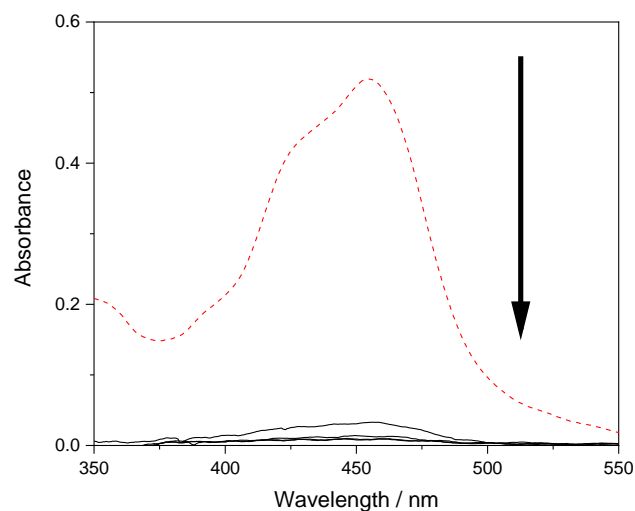


Fig. S18 UV-vis spectra of a tris(2,2'-bipyridyl)ruthenium(II) chloride (Rubpy)-doped PVA/DBA film on on a polystyrene Petri dish before (broken line) and after immersion in water (solid lines, immersion time: 5, 20, 60 and 120 min). A PVA/DBA-coated PS Petri dish was used as a reference for the measurements.

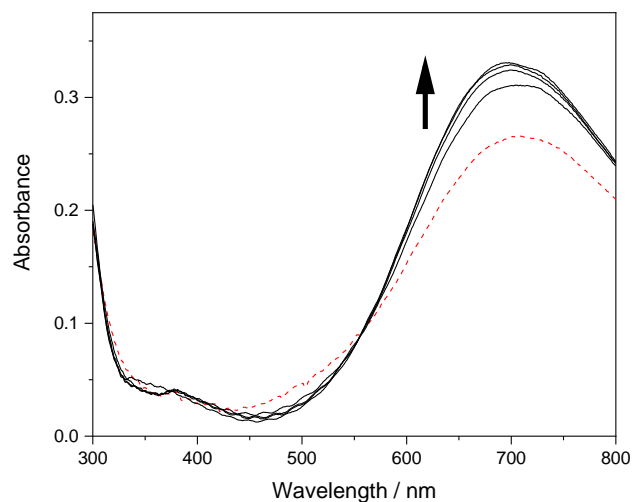


Fig. S19 UV-vis spectra of a Prussian blue (PB)-doped PVA/DBA film on a polystyrene Petri dish before (broken line) and after immersion in water (solid lines, immersion time: 2 h, 6 h, 12 h and 24 h). A PVA/DBA-coated PS Petri dish was used as a reference for the measurements. The observed increase of the absorption at 698 nm accompanied with the decrease of the absorption at 500 nm during the immersion is ascribable to an equilibrium shift from partially reduced iron(II) hexacyanoferrate(II) (Prussian white) to stable iron(III) hexacyanoferrate(II) (PB) in the film.

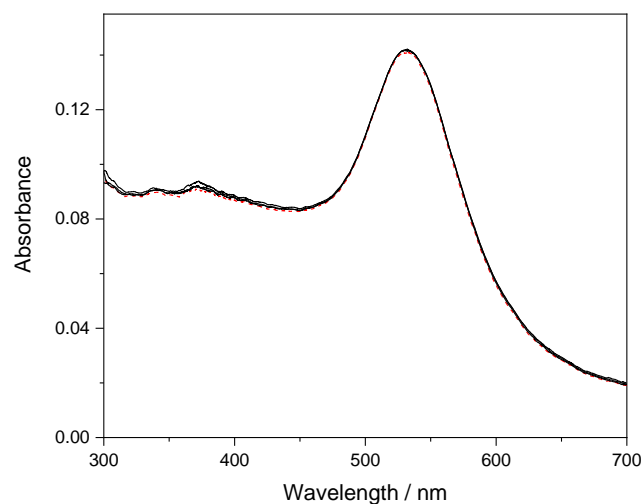


Fig. S20 UV-vis spectra of a gold nanoparticle (AuNPs)-doped PVA/DBA film on a polystyrene Petri dish before (broken line) and after immersion in water (solid lines, immersion time: 2 h, 12 h and 24 h). A PVA/DBA-coated PS Petri dish was used as a reference for the measurements.



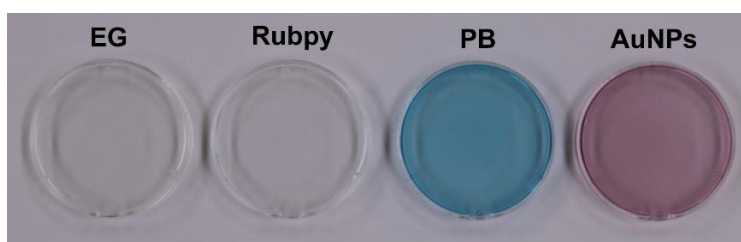


Fig. S21 Photographs of the composite coating films on PS Petri dishes after immersion in water for 24 h.

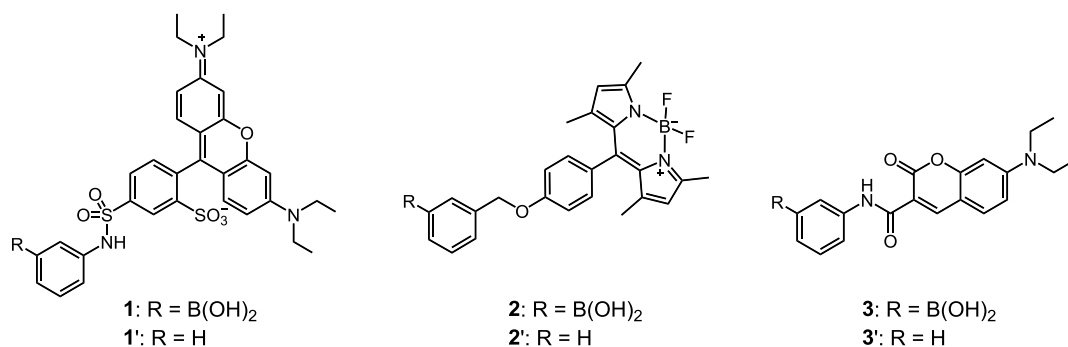


Fig. S22 Chemical structures of fluorescent dyes employed for the evaluation of the secondary functionalization reactivity of the PVA/DBA film.

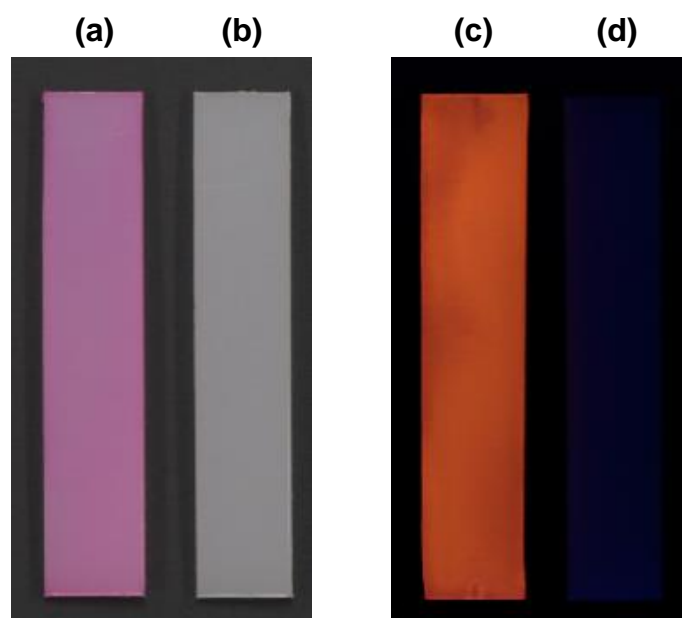


Fig. S23 Photographs of PVA/DBA-coated PE substrate treated with **1** (a and c) and **1'** (b and d). The photographs were taken under ambient light (a and b) and UV-light at 365 nm (c and d). Photographic conditions: exposure time = 1/80 (f/5.6, ISO400) under ambient light and exposure time = 1/2 (f/5, ISO400) under UV-light.

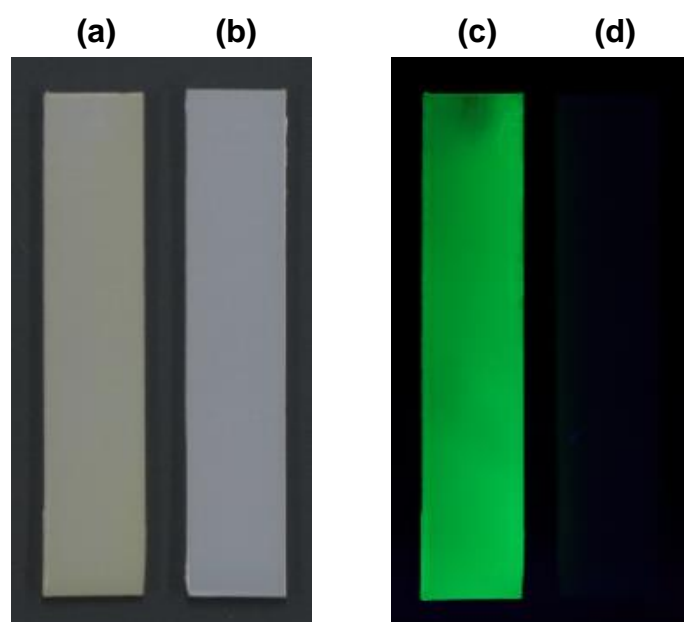


Fig. S24 Photographs of PVA/DBA-coated PE substrate treated with **2** (a and c) and **2'** (b and d). The photographs were taken under ambient light (a and b) and UV-light at 365 nm (c and d). Photographic conditions: exposure time = 1/80 (f/5.6, ISO400) under ambient light and exposure time = 1/2 (f/5, ISO400) under UV-light. The quantum yield of the functionalized coated PE substrate with **2** was determined to be 60%.

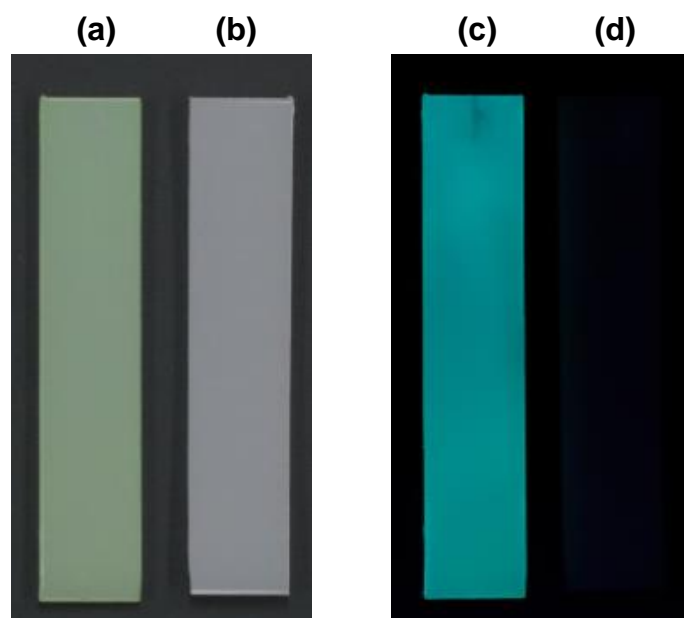


Fig. S25 Photographs of PVA/DBA-coated PE substrates treated with **3** (a and c) and **3'** (b and d). The photographs were taken under ambient light (a and b) and UV-light at 365 nm (c and d). Photographic conditions: exposure time = 1/80 (f/5.6, ISO400) under ambient light and exposure time = 1/2 (f/5, ISO400) under UV-light. The quantum yield of the functionalized coated PE substrate with **3** was determined to be 62%.

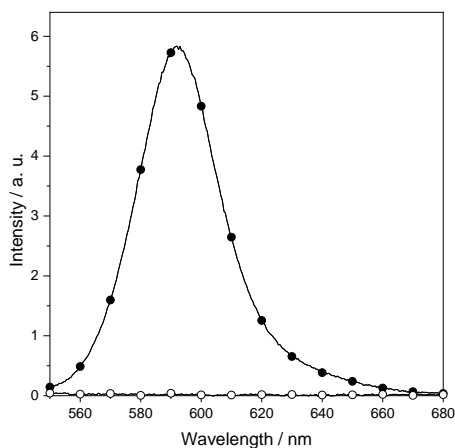


Fig. S26 Fluorescence spectra of PVA/DBA-coated PE substrates treated with **1** (filled circle) and **1'** (open circle).  $\lambda_{\text{ex}} = 540 \text{ nm}$ .

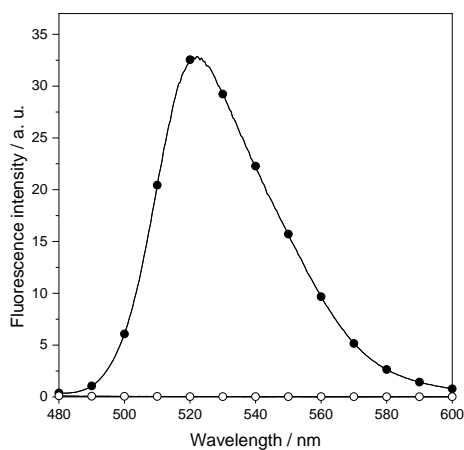


Fig. S27 Fluorescence spectra of PVA/DBA-coated PE substrates treated with **2** (filled circle) and **2'** (open circle).  $\lambda_{\text{ex}} = 470 \text{ nm}$ .

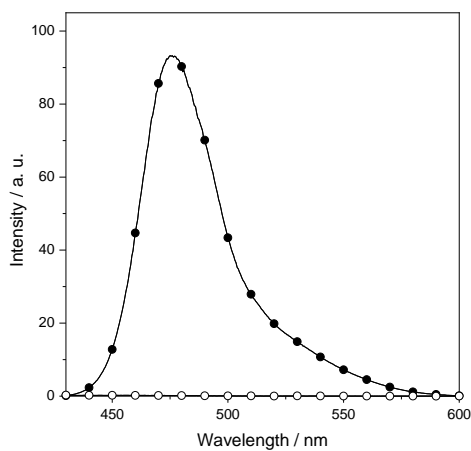


Fig. S28 Fluorescence spectra of PVA/DBA-coated PE substrates treated with **3** (filled circle) and **3'** (open circle).  $\lambda_{\text{ex}} = 420 \text{ nm}$ .

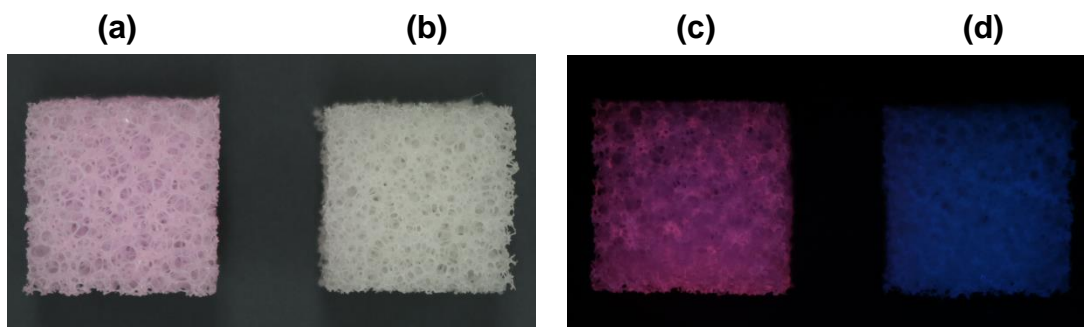


Fig. S29 Photographs of PVA/DBA-coated polyurethane sponges treated with **1** (a and c) and **1'** (b and d). The photographs were taken under ambient light (a and b) and UV-light at 365 nm (c and d). Photographic conditions: exposure time = 1/100 (f/5.6, ISO400) under ambient light and exposure time = 1/4 (f/5.6, ISO400) under UV-light.

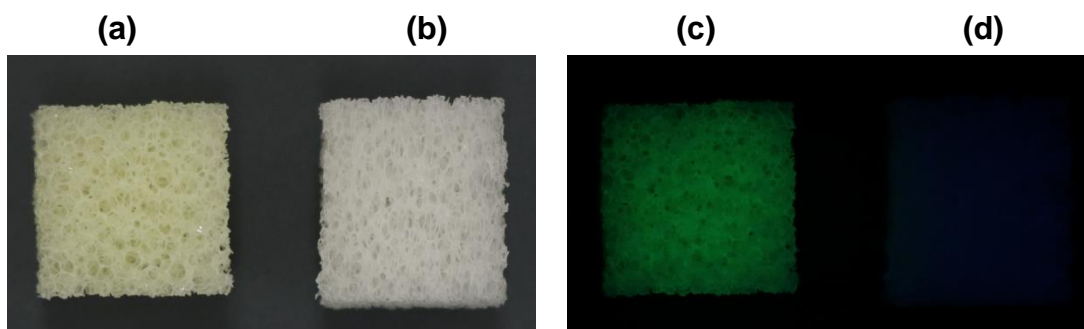


Fig. S30 Photographs of PVA/DBA-coated polyurethane sponges treated with **2** (a and c) and **2'** (b and d). The photographs were taken under ambient light (a and b) and UV-light at 365 nm (c and d). Photographic conditions: exposure time = 1/100 (f/5.6, ISO400) under ambient light and exposure time = 1/20 (f/5, ISO400) under UV-light.

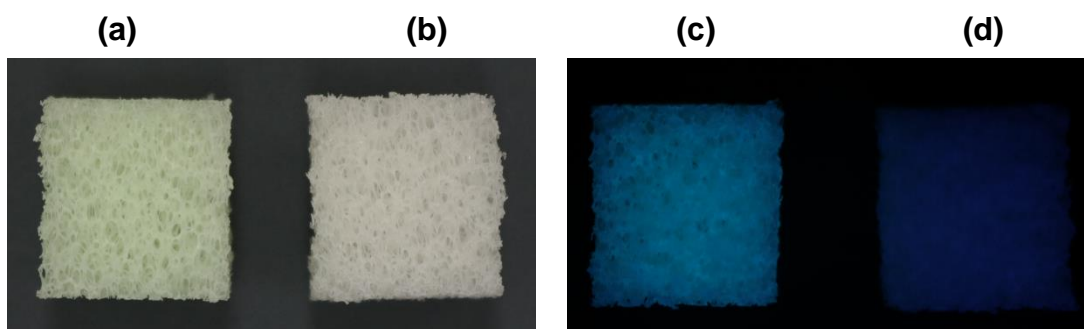


Fig. S31 Photographs of PVA/DBA-coated polyurethane sponges treated with **3** (a and c) and **3'** (b and d). The photographs were taken under ambient light (a and b) and UV-light at 365 nm (c and d). Photographic conditions: exposure time = 1/100 (f/5.6, ISO400) under ambient light and exposure time = 1/8 (f/5, ISO400) under UV-light.

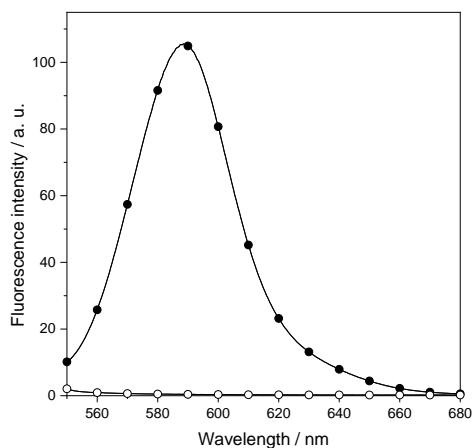


Fig. S32 Fluorescence spectra of PVA/DBA-coated polyurethane sponges treated with **1** (filled circle) and **1'** (open circle).  $\lambda_{\text{ex}} = 540 \text{ nm}$ .

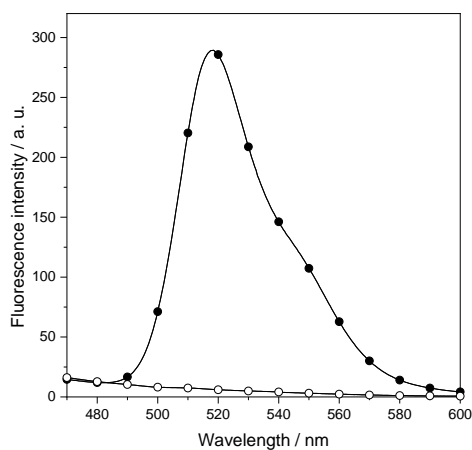


Fig. S33 Fluorescence spectra of PVA/DBA-coated polyurethane sponges treated with **2** (filled circle) and **2'** (open circle).  $\lambda_{\text{ex}} = 365 \text{ nm}$ .

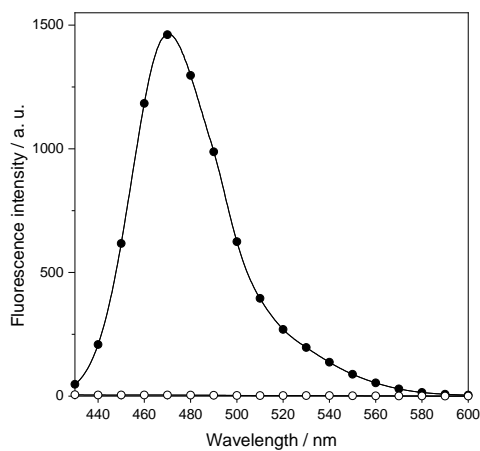


Fig. S34 Fluorescence spectra of PVA/DBA-coated polyurethane sponges treated with **3** (filled circle) and **3'** (open circle).  $\lambda_{\text{ex}} = 420 \text{ nm}$ .

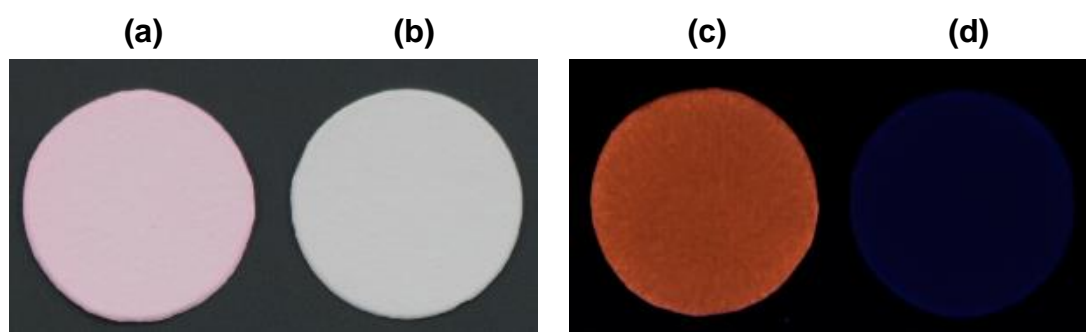


Fig. S35 Photographs of PVA/DBA-coated glass fiber filter papers treated with **1** (a and c) and **1'** (b and d). The photographs were taken under ambient light (a and b) and UV-light at 365 nm (c and d). Photographic conditions: exposure time = 1/80 (f/5.6, ISO400) under ambient light and exposure time = 1/2 (f/5, ISO400) under UV-light. The quantum yield of the functionalized coated filter with **1** was determined to be 82 %.

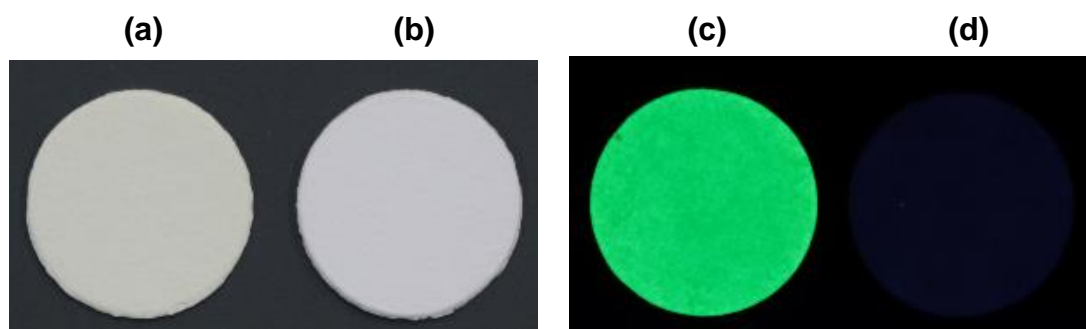


Fig. S36 Photographs of PVA/DBA-coated glass fiber filter papers treated with **2** (a and c) and **2'** (b and d). The photographs were taken under ambient light (a and b) and UV-light at 365 nm (c and d). Photographic conditions: exposure time = 1/80 (f/5.6, ISO400) under ambient light and exposure time = 1/2 (f/5, ISO400) under UV-light. The quantum yield of the functionalized coated filter with **2** was determined to be 88 %.

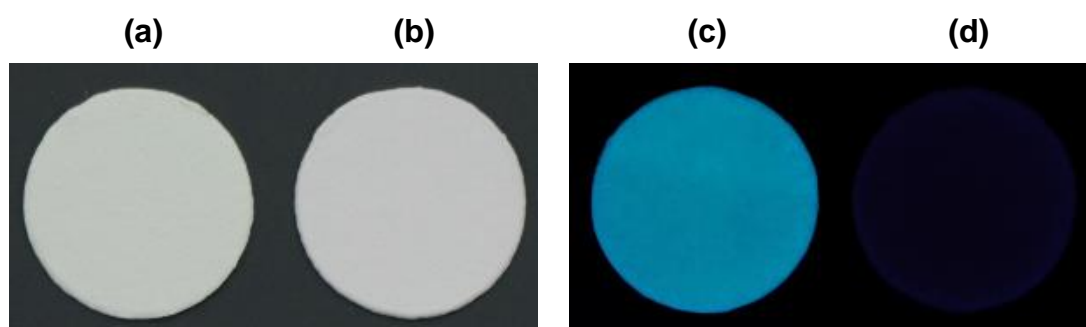


Fig. S37 Photographs of PVA/DBA-coated glass fiber filter papers treated with **3** (a and c) and **3'** (b and d). The photographs were taken under ambient light (a and b) and UV-light at 365 nm (c and d). Photographic conditions: exposure time = 1/80 (f/5.6, ISO400) under ambient light and exposure time = 1/2 (f/5, ISO400) under UV-light. The quantum yield of the functionalized coated filter with **3** was determined to be 82 %.

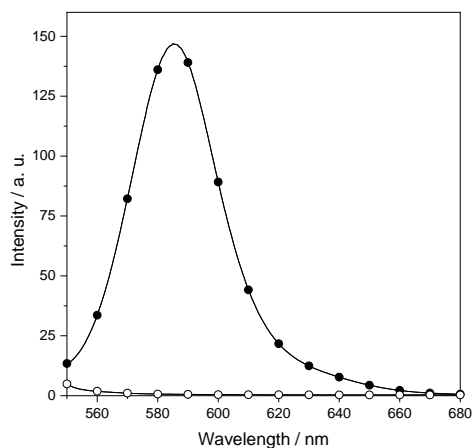


Fig. S38 Fluorescence spectra of PVA/DBA-coated glass fiber filter papers treated with **1** (filled circle) and **1'** (open circle).  $\lambda_{\text{ex}} = 540 \text{ nm}$ .

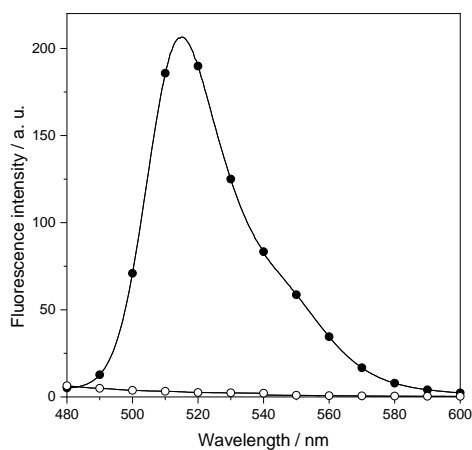


Fig. S39 Fluorescence spectra of PVA/DBA-coated glass fiber filter papers treated with **2** (filled circle) and **2'** (open circle).  $\lambda_{\text{ex}} = 365 \text{ nm}$ .

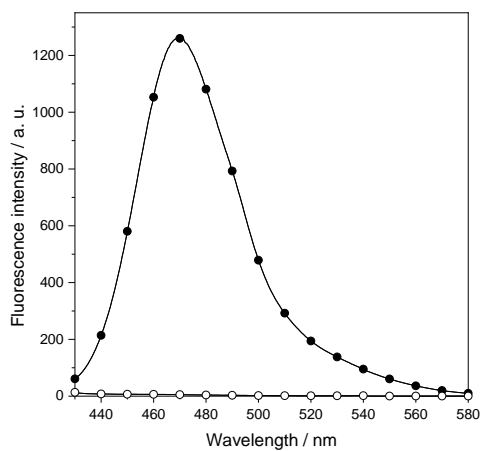


Fig. S40 Fluorescence spectra of PVA/DBA-coated glass fiber filter papers treated with **3** (filled circle) and **3'** (open circle).  $\lambda_{\text{ex}} = 420 \text{ nm}$ .

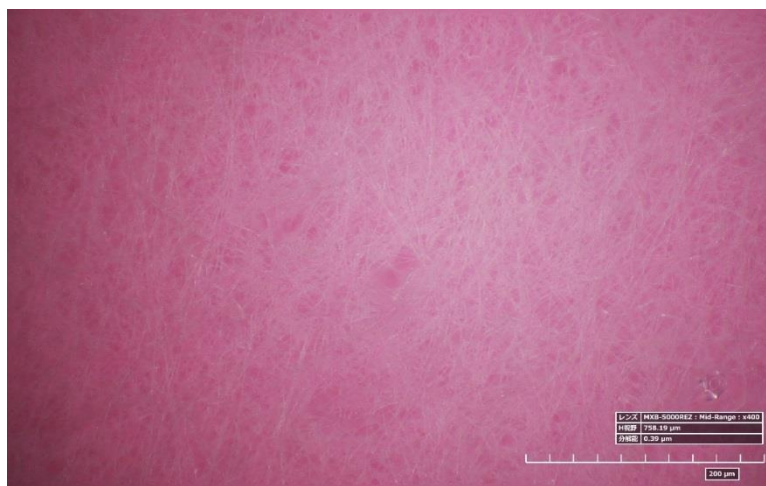


Fig. S41 Digital microscope image of a PVA/DBA-coated glass fiber filter treated with **1**.

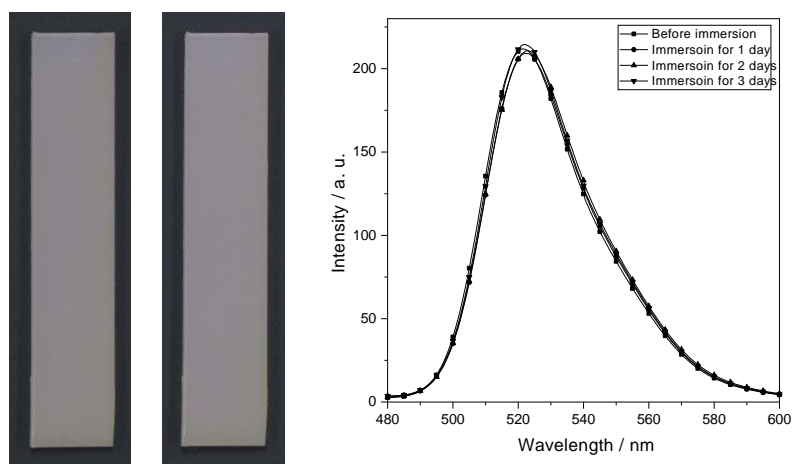


Fig. S42 Photographs a PVA/DBA-coated PE substrate functionalized with **2** before (left) and after (right) immersion in water and the corresponding fluorescence spectra ( $\lambda_{\text{ex}} = 366 \text{ nm}$ ).



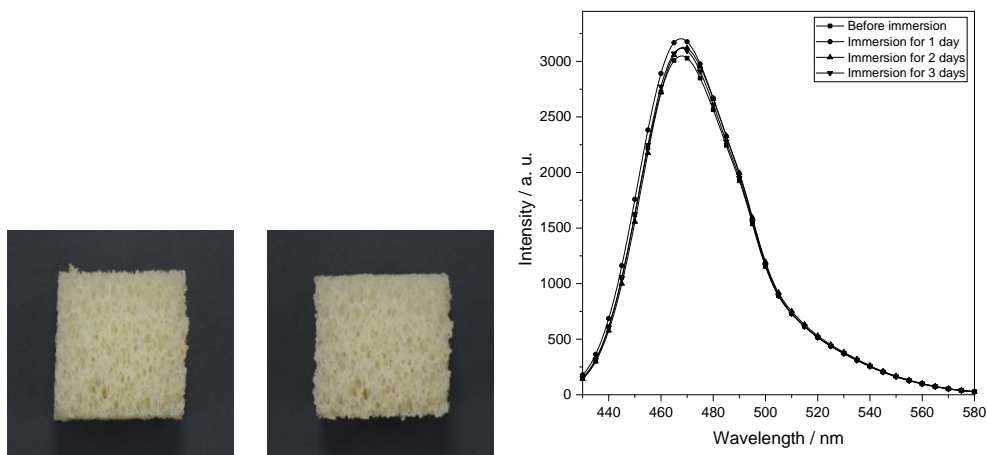


Fig. S43 Photographs of a PVA/DBA-coated polyurethane sponge functionalized with **3** before (left) and after (right) immersion in water and the corresponding fluorescence spectra ( $\lambda_{\text{ex}} = 420 \text{ nm}$ ).

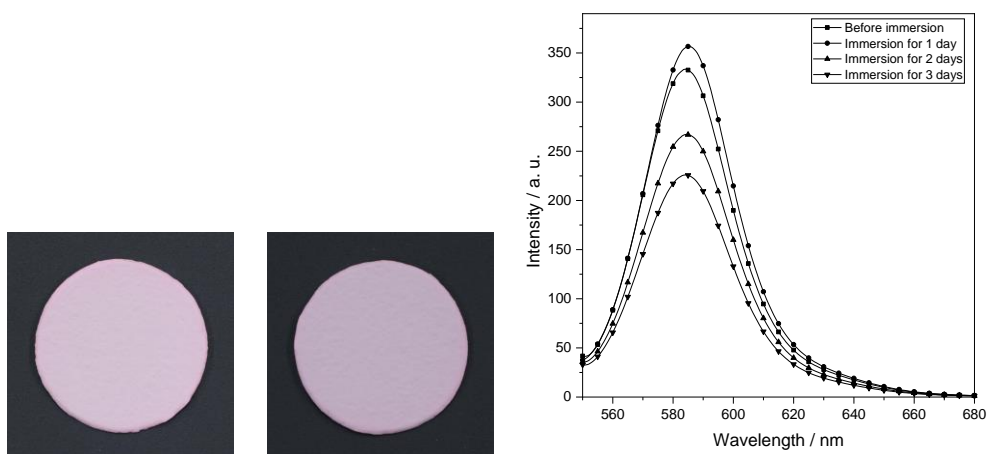


Fig. S44 Photographs and spectra of a PVA/DBA-coated glass fiber filter paper functionalized with **1** before (left) and after (right) immersion in water and the corresponding fluorescence spectra ( $\lambda_{\text{ex}} = 540 \text{ nm}$ ). The decrease of the fluorescent intensity is probably due to the falling out of the glass fibers from the filter during the immersion processes.

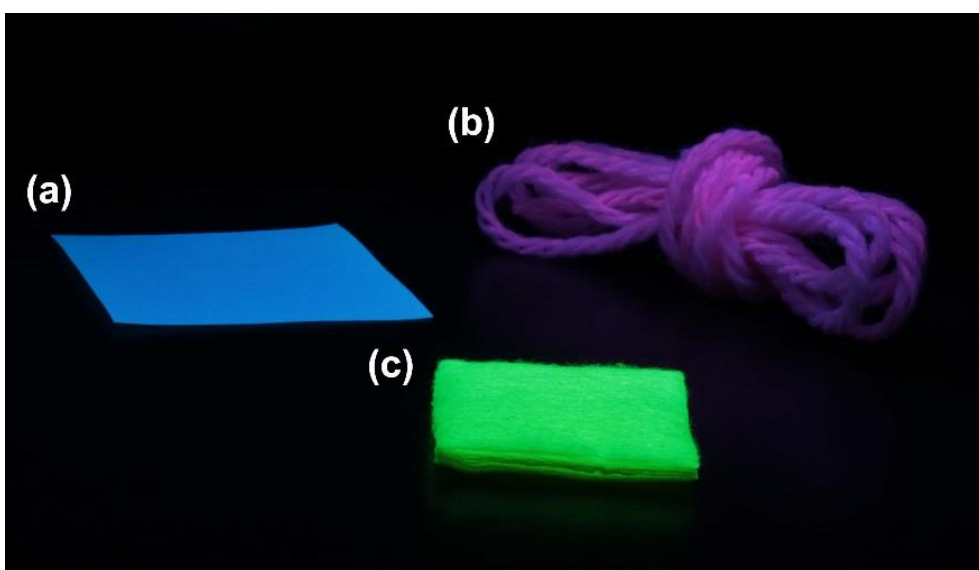
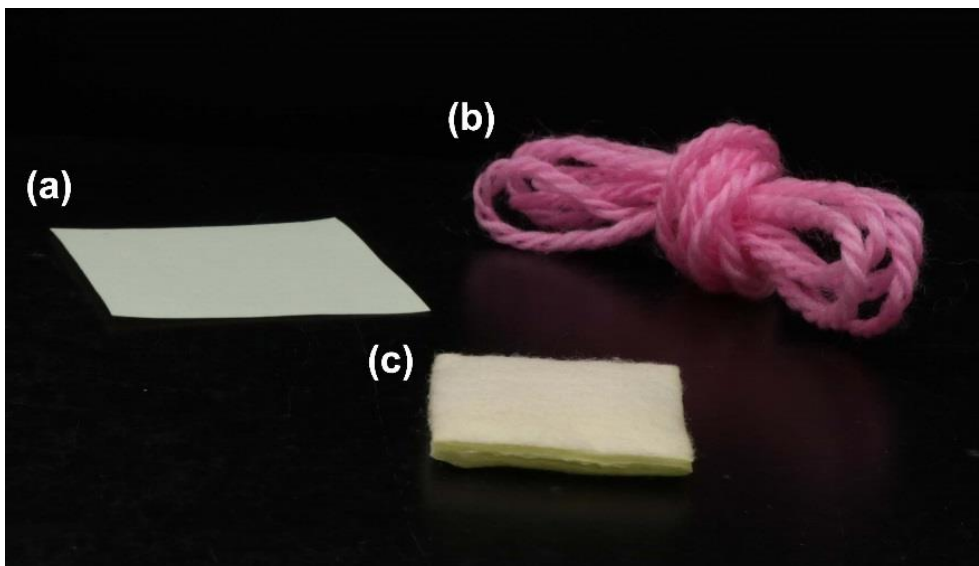


Fig. S45 Photographs of secondary functionalized PVA/DBA-coated drawing paper with **3** (a), PVA/DBA-coated wool yarn with **1** (b) and PVA/DBA-coated cotton pad with **2** (c). These photographs were taken under ambient light (top) and UV-light (bottom), respectively.

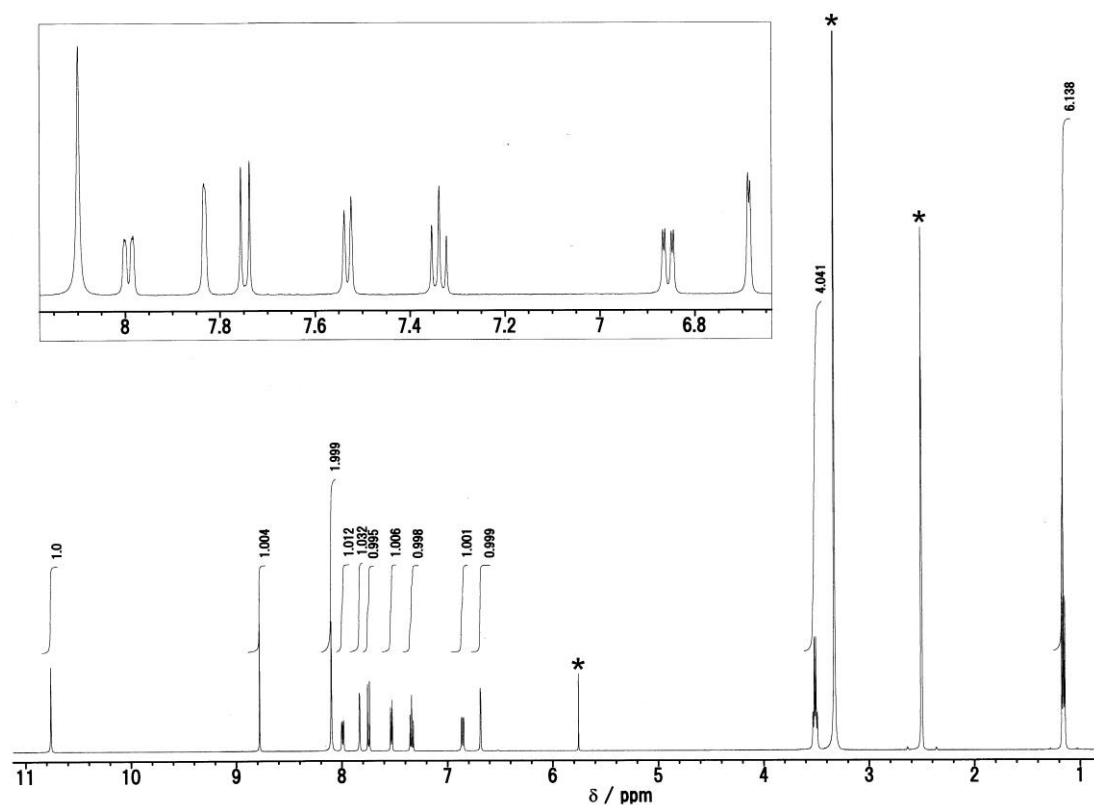


Fig. S46  $^1\text{H}$  NMR (500 MHz) spectrum of **3** in  $\text{DMSO-}d_6$ . Inset: Enlarged  $^1\text{H}$ -NMR spectrum in a region of a low magnetic field. The solvent peaks (5.76 ppm: dichloromethane and 2.50 ppm: dimethyl sulfoxide) and water peak (3.33 ppm) are marked with asterisks.

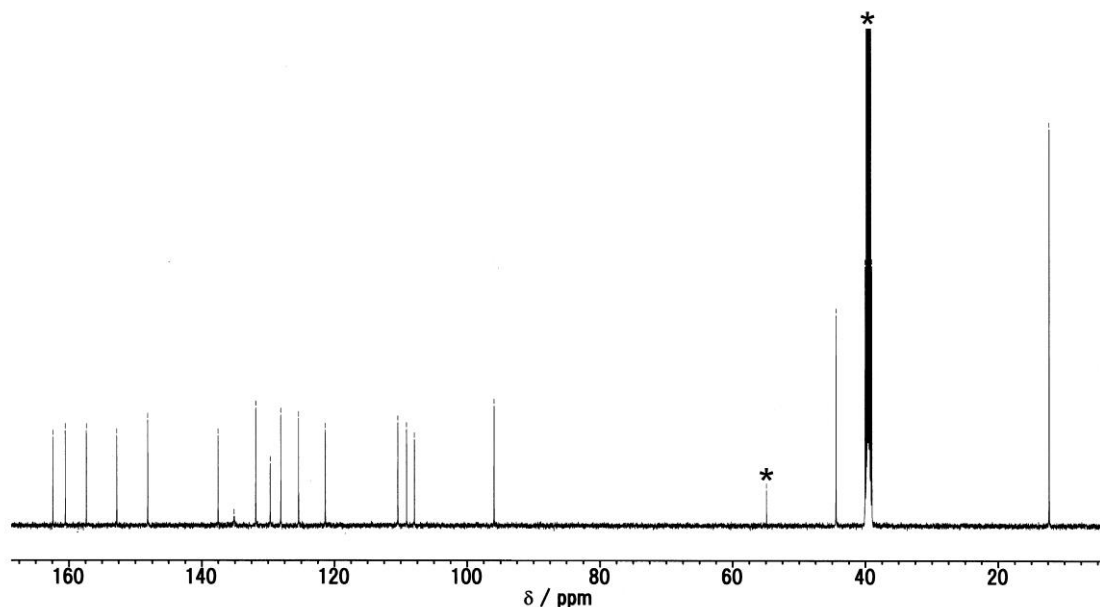


Fig. S47  $^{13}\text{C}$  NMR (126 MHz) spectrum of **3** in  $\text{DMSO-}d_6$ . The solvent peaks are marked with asterisks (54.9 ppm: dichloromethane and 39.7 ppm: dimethyl sulfoxide).

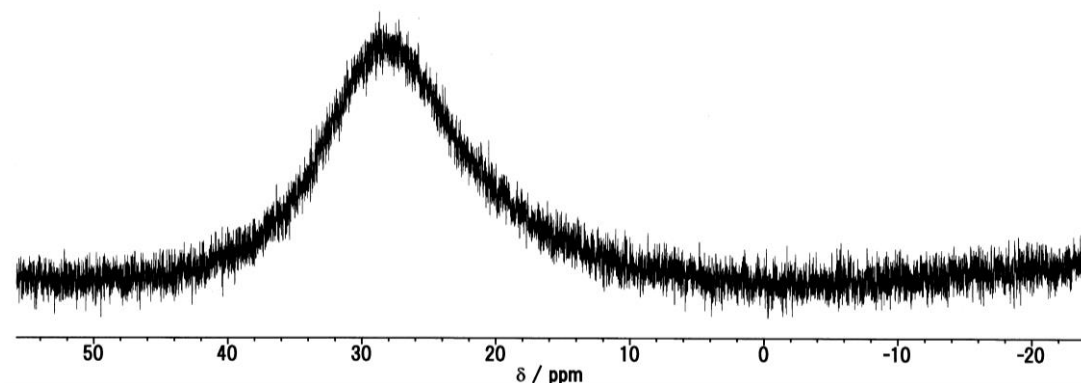


Fig. S48  $^{11}\text{B}$  NMR (160 MHz) spectrum of **3** in  $\text{DMSO-}d_6$ .

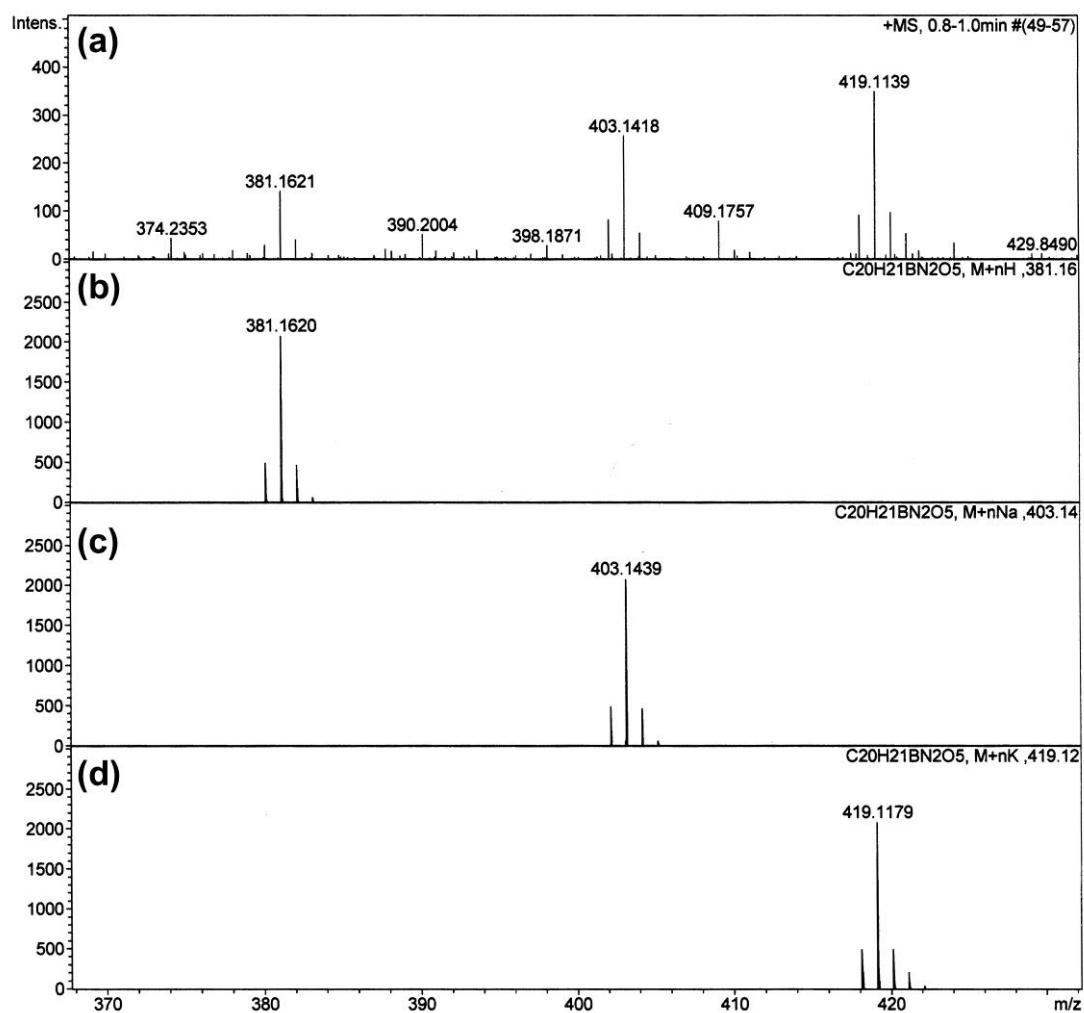


Fig. S49 (a) HRMS (ESI) of **3** and simulated isotope patterns of (b)  $[\mathbf{3} + \text{H}]^+$ , (c)  $[\mathbf{3} + \text{Na}]^+$ , and (d)  $[\mathbf{3} + \text{K}]^+$ .