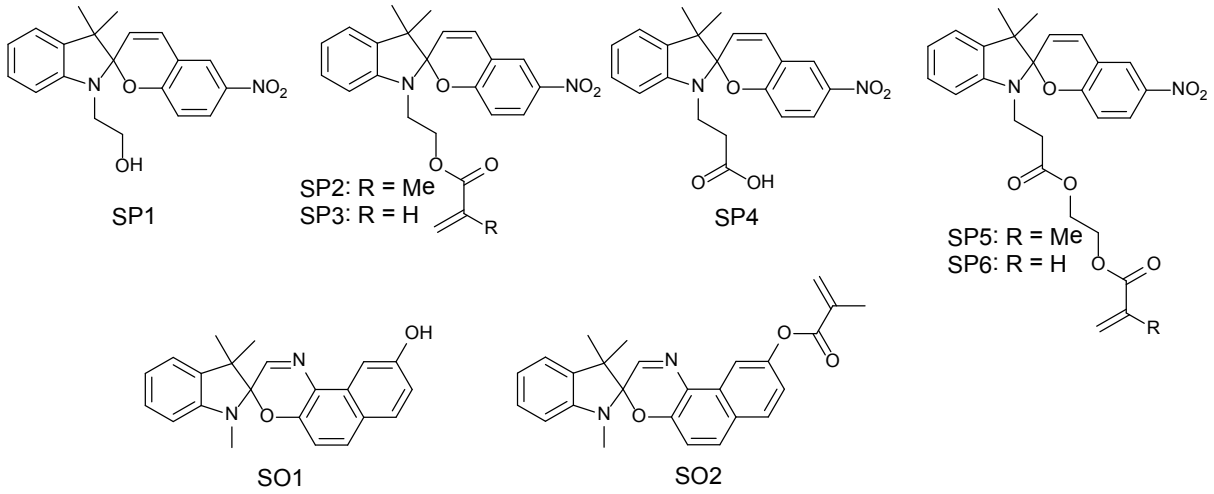
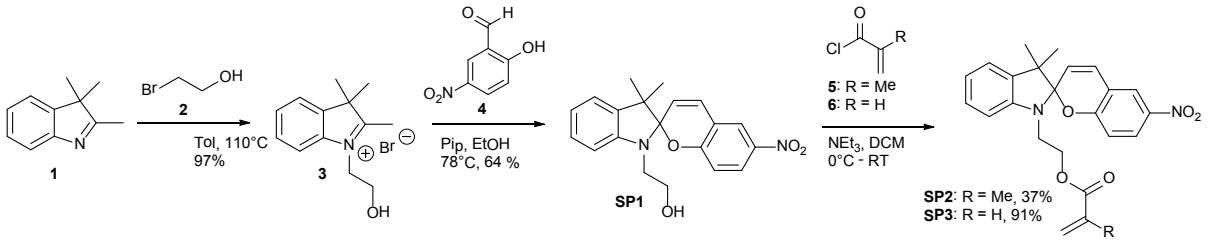
Electronic Supplementary Information

Photochromic compounds used in this study



Synthesis

Synthesis of spirobenzopyrans **SP2** and **SP3**



1-(2-hydroxyethyl)-2,3,3-trimethyl-3H-indol-1-ium bromide (3). A dry round-bottom flask was charged with indoline **1** (5.0 g, 31 mmol) and 50 mL toluene. After addition of bromide **2** (4.7 g, 38 mmol) the reaction mixture was heated to 110°C and stirred for 12 h. After cooling to room temperature, the precipitated material was isolated by vacuum filtration and washed with cold toluene followed by Et_2O to obtain product **3** (8.7 g, 30 mmol, 97%) as a light pink salt.
^{1}H-NMR (400 MHz, d_6-DMSO) δ: 7.98 (dd, J = 5.6, 3.4 Hz, 1H, H7), 7.85 (dd, J = 5.8, 2.9 Hz, 1H, H4), 7.63 – 7.55 (m, 2H, H5, H6), 4.64 – 4.58 (t, J = 5.1 Hz, 2H, HA), 3.90 – 3.84 (t, J = 5.1 Hz, 2H, HB), 2.83 (s, 3H, C2-**Me**), 1.55 (s, 6H, C3-**Me$_2$**).
^{13}C-NMR (101 MHz, d_6-DMSO) δ: 197.73 (C2), 141.80 (C3a), 141.14 (C7a), 129.27 (C6), 128.78 (C5), 123.45 (C4), 115.61 (C7), 57.74 (CB), 54.24 (C3), 50.31 (CA), 22.01 (2C, C3-**Me$_2$**), 14.50 (C2-**Me**).
IR (cm^{-1}): 3251, 1607, 1463, 1379, 1092, 1062, 721.
LRMS-ESI$_{pos}$ (*m/z*): $[M-Br]^+$ calc. for $C_{13}H_{18}NO$ 204.1; found 203.7.

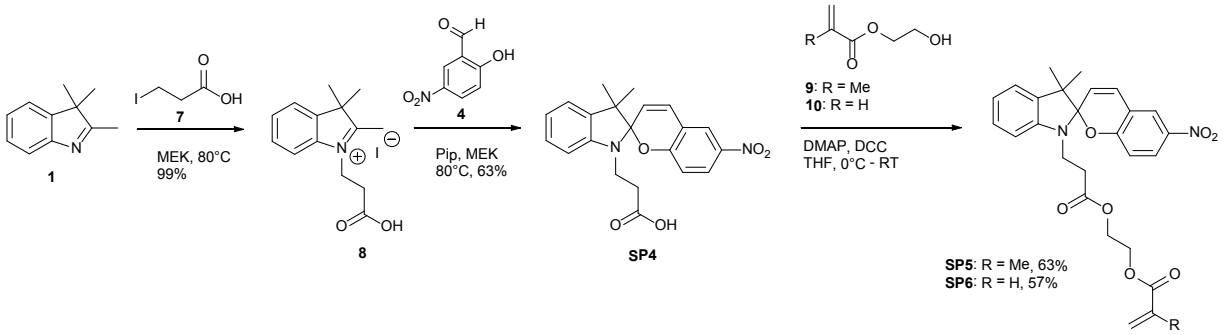
2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethanol (SP1). Bromide salt **3** (2.0 g, 7.0 mmol) was dissolved in 20 mL ethanol. Piperidine (0.77 mL, 7.7 mmol) and benzaldehyde **4** (1.78 g, 10.7 mmol) were added in one portion. The reaction mixture was refluxed for 5 h. After cooling to room temperature, the mixture was stirred for an additional hour. Precipitated material was then isolated at 0°C and washed with cold ethanol to obtain spiropyran **SP1** (1.6 g, 4.5 mmol, 64%) as violet powder.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.02 (m, 2H, H5, H7), 7.20 (dd, *J* = 7.8, 7.6 Hz, 1H, H6'), 7.11 (d, *J* = 7.1 Hz, 1H, H4'), 6.91 (m, 2H, H4, H5'), 6.77 (d, *J* = 8.7 Hz, 1H, H8), 6.68 (d, *J* = 7.8 Hz, 1H, H7'), 5.90 (d, *J* = 10.4 Hz, 1H, H3), 3.91 – 3.67 (m, 2H, HA), 3.58 – 3.42 (m, 1H, HB), 3.41 – 3.28 (m, 1H, HB), 1.30 (s, 3H, C3'-**Me$_2$**), 1.20 (s, 3H, C3'-**Me$_2$**).
^{13}C-NMR (101 MHz, $CDCl_3$) δ: 159.28 (C8a), 146.93 (C7a'), 141.10 (C6), 135.78 (C3a'), 128.22 (C4), 127.81 (C6'), 125.93 (C7), 122.73 (C5), 121.90 (2C, C3 and C4'), 119.95 (C5'), 118.51 (C4a), 115.49 (C8), 106.87 (C7'), 106.69 (C2), 60.81 (CA), 52.80 (C3'), 46.07 (CB), 25.87 (C3'-**Me$_2$**), 19.98 (C3'-**Me$_2$**).
IR (cm^{-1}): 2958, 2926, 1609, 1480, 1334, 1272, 1088, 952, 722.
UV/VIS (MeCN): ε_{366} = 2684 $M^{-1}cm^{-1}$ $\lambda_{max,UV}$ = 560 nm
LRMS-ESI$_{pos}$ (*m/z*): $[MH]^+$ calc. for $C_{20}H_{21}N_2O_4$ 353.1; found 352.9

2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethyl methacrylate (SP2). A dry round-bottom flask was charged with spiropyran **SP1** (5.0 g, 14.2 mmol) and 40 mL DCM. After wrapping the flask with aluminum foil, the reaction mixture was cooled to 0°C. NEt_3 (2.4 mL, 17.0 mmol) was added in one portion followed by drop-wise addition of acid chloride **5** (1.7 mL, 17.0 mmol). After keeping the reaction at 0°C for an additional hour, the mixture was stirred at room temperature for 12 h.
Purification by column chromatography (3:2 DCM:Hx) allowed isolation of methacrylate **SP2** (2.2 g, 5.2 mmol, 37%) as dark-red, sticky substance.
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.09 – 7.93 (m, 2H, H5, H7), 7.21 (dd, *J* = 7.7, 7.5 Hz, 1H, H6'), 7.09 (d, *J* = 7.3 Hz, 1H, H4'), 6.94 – 6.83 (m, 2H, H4, H5'), 6.76 (d, *J* = 8.2 Hz, 1H, H8), 6.70 (d, *J* = 7.7 Hz, 1H, H7') 6.07 (s, 1H, CE=**CH$_2$**), 5.88 (d, *J* = 10.3 Hz, 1H, H3), 5.56 (s, 1H, CE=**CH$_2$**), 4.30 (m, 2H, HB), 3.60 – 3.40 (m, 2H, HA), 1.92 (s, 3H, CE-**Me**), 1.28 (s, 3H, C3'-**Me$_2$**), 1.16 (s, 3H, C3'-**Me$_2$**).
^{13}C-NMR (101 MHz, $CDCl_3$) δ: 167.33 (CD), 159.53 (C8a), 146.79 (C7a'), 141.22 (C6), 136.17 (CE), 135.83 (C3a'), 128.43 (C4), 127.98 (C6'), 126.07 (2C, C7 and CE=**CH2**), 122.91 (C5), 121.93 (2C, C3 and C4') 120.06 (C5'), 118.55 (C4a), 115.69 (C8), 106.89 (C7'), 106.65 (C2), 62.76 (CB), 52.94 (C3'), 42.56 (CA), 25.97 (C3'-**Me$_2$**), 19.96 (C3'-**Me$_2$**), 18.48 (CE-**Me**).
IR (cm^{-1}): 2927, 1734, 1608, 1522, 1456, 1336, 1089, 1025, 950, 744.
UV/VIS (MeCN): ε_{366} = 1776 $M^{-1}cm^{-1}$ $\lambda_{max,UV}$ = 565 nm
LRMS-ESI$_{pos}$ (*m/z*): $[MH]^+$ calc. for $C_{24}H_{25}N_2O_5$ 421.2; found 421.2
EA: calc. [C] 68.6%, [H] 5.8%, [N] 6.7%; found [C] 67.2%, [H] 5.7%, [N] 6.3%.

2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethyl acrylate (SP3). Spiropyran **SP1** (5.6 g, 15.9 mmol) was dissolved in 50 mL DCM. After wrapping the flask with aluminum foil, the reaction mixture was cooled to 0°C. NEt_3 (2.8 mL, 19.1 mmol) was added in one portion followed by drop-wise addition of acid chloride **6** (1.6 mL, 19.1 mmol). After stirring for an additional hour at 0°C the reaction mixture was stored for 12 h at room temperature. The crude product was then dissolved in DCM and washed with 0.1 M HCl solution, saturated $NaHCO_3$ solution and brine. Acrylate **SP3** (5.9 g, 14.5 mmol, 91%) was isolated as a red sticky substance.
^{1}H-NMR (400 MHz, d_6-DMSO) δ: 8.20 (s, 1H, H5), 7.98 (d, *J* = 9.0 Hz, 1H, H7), 7.18 (d, *J* = 10.4 Hz, 1H, H4), 7.12 (m, 2H, H4', H6'), 6.86 (d, *J* = 9.0 Hz, 1H, H8), 6.78 (dd, *J* = 7.3, 7.3 Hz, 1H, H5'), 6.71 (d, *J* = 7.9 Hz, 1H H7'), 6.26 (d, *J* = 17.2 Hz, 1H, CE=**CH$_2$**), 6.09 (dd, *J* = 17.2, 10.3 Hz, 1H, CE-**H**), 5.97 (d, *J* = 10.4 Hz, 1H, H3), 5.89 (d, *J* = 10.3 Hz, 1H, CE=**CH$_2$**), 4.35 – 4.15 (m, 2H, HB), 3.70 – 3.25 (m, 2H, HA), 1.18 (s, 3H, C3'-**Me$_2$**), 1.06 (s, 3H, C3'-**Me$_2$**).
^{13}C-NMR (101 MHz, d_6-DMSO) δ: 165.30 (CD), 159.05 (C8a), 146.35 (C7a'), 140.55 (C6), 135.42 (C3a'), 131.70 (CE=**CH$_2$**), 128.12 (2C, C4 and CE), 127.58 (C4' or C6'), 125.73 (C7), 122.83 (C5), 121.63 (2C, C3 and C4' or CC6'), 119.37 (C5'), 118.71 (C4a), 115.46 (C8), 106.52 (C7'), 106.23 (C2), 62.07 (CB), 52.36 (C3'), 41.87 (CA), 25.55 (C3'-**Me$_2$**), 19.44 (C3'-**Me$_2$**).
IR (cm^{-1}): 2960, 2927, 1719, 1479, 1333, 1272, 1185, 1089, 953, 805, 715.
UV/VIS (MeCN): ε_{366} = 3069 $M^{-1}cm^{-1}$ $\lambda_{max,UV}$ = 569 nm
LRMS-ESI$_{pos}$ (*m/z*): $[MH]^+$ calc. for $C_{23}H_{23}N_2O_5$ 406.2; found 406.9
EA: calc. [C] 68.0%, [H] 5.5%, [N] 6.9%; found [C] 68.5%, [H] 5.6%, [N] 7.1%.

Synthesis of spirobenzopyrans **SP5** and **SP6**



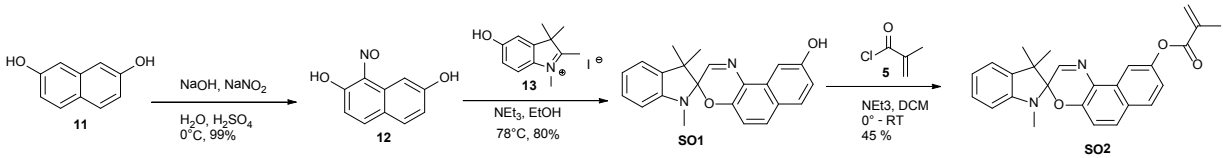
1-(2-carboxyethyl)-2,3,3-trimethyl-3H-indol-1-ium iodide (8). Indoline **1** (4.0 g, 25 mmol) was dissolved in 4 mL MEK. After addition of iodide **7** (5.4 g, 27 mmol) the reaction mixture was refluxed and stirred for 12 h. After cooling to room temperature, the precipitated material was isolated and washed with cold hexane followed by Et_2O to obtain iodide salt **8** (9.1 g, 25 mmol, 99%) as a light-brown salt.
^{1}H-NMR (400 MHz, d_6-DMSO) δ: 8.05 – 7.90 (dd, J = 5.8, 3.1 Hz, 1H, H7), 7.83 (dd, J = 4.0, 2.1 Hz, 1H, H4), 7.61 (m, 2H, H5, H6), 4.64 (t, J = 7.0 Hz, 2H, HA), 2.97 (t, J = 7.0 Hz, 2H, HB), 2.86 (s, 3H, C2-**Me**), 1.52 (s, 6H, C3-**Me$_2$**).
^{13}C-NMR (101 MHz, d_6-DMSO) δ: 197.88 (C2), 171.50 (CC), 141.73 (C3a), 140.80 (C8), 129.32 (C6), 128.89 (C5), 123.47 (C4), 115.55 (C7), 54.24 (C3), 43.55 (CB), 31.09 (CA), 21.86 (2C, C3-**Me$_2$**), 14.44 (C2-**Me**).
IR (cm^{-1}): 3032, 1727, 1397, 1171, 768.
LRMS-ESI$_{pos}$ (*m/z*): [M-I]$^+$ calc. for $C_{14}H_{18}NO_2$ 232.1; found 231.7

3-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)propanoic acid (SP4). A dry round-bottom flask was wrapped with aluminum foil and then charged with iodide salt **8** (4.5 g, 12.6 mmol) and 20 mL MEK. Piperidine (1.3 mL, 13.2 mmol) and benzaldehyde **4** (2.1 g, 12.6 mmol) were added in one portion. The reaction mixture was heated to 80°C and stirred for 3 h. Then the reaction mixture was cooled to room temperature and stored for 12 h without stirring. After cooling to 0°C, the precipitated material was isolated and washed with cold MEK followed by MeOH to obtain spiropyran **SP4** (3.0 g, 7.9 mmol, 63%) as yellow powder.
^{1}H-NMR (400 MHz, d_6-DMSO) δ: 12.22 (s, 1H, COO**H**), 8.20 (s, 1H, H5), 7.99 (d, J = 9.0 Hz, 1H, H7), 7.20 (d, J = 10.4 Hz, 1H, H4), 7.10 (m, 2H, H4', H6'), 6.85 (d, J = 9.0 Hz, 1H, H8), 6.79 (dd, J = 7.4, 7.4 Hz, 1H, H5'), 6.65 (d, J = 8.0 Hz, 1H, H7'), 5.98 (d, J = 10.4 Hz, 1H, H3), 3.60 – 3.21 (m, 2H, HA), 2.66 – 2.26 (m, 2H, HB), 1.17 (s, 3H, C3-**Me$_2$**), 1.06 (s, 3H, C3-**Me$_2$**).
^{13}C-NMR (101 MHz, d_6-DMSO) δ: 172.85 (CC), 159.07 (C8a), 146.10 (C7a'), 140.54 (C6), 135.64 (C3a'), 128.15 (C4), 127.63 (C4' or C6)', 125.70 (C7), 122.79 (C5), 121.77 (2C, C3 and C4' or C6'), 119.22 (C5'), 118.83 (C4a), 115.48 (C8), 106.63 (C7'), 106.49 (C2), 52.41 (CA), 38.85 (C3'), 33.15 (CB), 25.57 (C3'-**Me$_2$**), 19.45 (C3'-**Me$_2$**).
IR (cm^{-1}): 1705, 1480, 1328, 1268, 944, 914, 747.
UV/VIS (MeCN): ε_{366} = 1387 M^{-1}cm^{-1} $\lambda_{max,UV}$ = 565 nm
LRMS-ESI$_{pos}$ (*m/z*): [MH]$^+$ calc. for $C_{21}H_{21}N_2O_5$ 381.1; found 380.9

2-((3-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)propanoyl)oxy)ethyl methacrylate (SP5). Spiropyran **SP4** (2.0 g, 5.3 mmol), HEMA **9** (0.67 g, 5.8 mmol) and DMAP (122 mg, 1.0 mmol) were dissolved in 50 mL THF. After cooling to 0°C, DCC (1.2 g, 5.8 mmol) was added in one portion. The reaction mixture was then stirred at room temperature for additional 12 h. After removing the solvent, the crude mixture was dissolved in DCM and washed with brine. Recrystallization from EtOAc/Hx resulted in product **SP5** (1.6 g, 3.3 mmol, 63%) as yellow crystals.
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.03 – 7.98 (m, 2H, H5, H7), 7.19 (dd, J = 7.7, 7.5 Hz, 1H, H6'), 7.09 (d, J = 7.3 Hz, 1H, H4'), 6.95 – 6.88 (m, 2H, H4, H5'), 6.73 (d, J = 8.3 Hz, 1H, H8), 6.61 (d, J = 7.7 Hz, 1H, H7'), 6.08 (s, 1H, CI=**CH$_2$**), 5.86 (d, J = 10.4 Hz, 1H, H3), 5.56 (s, 1H, CI=**CH$_2$**), 4.32 – 4.23 (m, 4H, HE, HF), 3.70 – 3.47 (m, 2H, HA), 2.78 – 2.55 (m, 2H, HB), 1.91 (s, 3H, CI-**Me**), 1.26 (s, 3H, C3'-**Me$_2$**), 1.14 (s, 3H, C3'-**Me$_2$**).
^{13}C-NMR (101 MHz, $CDCl_3$) δ: 171.69 (CC), 167.15 (CH), 159.47 (C8a), 146.30 (C7a'), 141.19 (C6), 136.08 (C3a'), 135.96 (CI), 128.48 (C4), 127.92 (C6'), 126.10 (2C, C7 and CI=**CH2**), 122.87 (C5), 122.03 (2C, C3 and C4'), 119.99 (C5'), 118.71 (C4a), 115.64 (C8), 106.86 (2C, C2 and C7'), 62.40 (2C, CE and CF), 53.04 (C3'), 39.29 (CA), 33.55 (CB), 25.86 (C3'-**Me$_2$**), 19.88 (C3'-**Me$_2$**), 18.35 (CI-**Me**).
IR (cm^{-1}): 2929, 1728, 1480, 1328, 1272, 1155, 946, 746.
UV/VIS (MeCN): ε_{366} = 1219 M^{-1}cm^{-1} $\lambda_{max,UV}$ = 566 nm
LRMS-ESI$_{pos}$ (*m/z*): [MH]$^+$ calc. for $C_{27}H_{29}N_2O_7$ 493.2; found 493.0
EA: calc. [C] 65.8%, [H] 5.7%, [N] 5.7%; found [C] 66.4%, [H] 5.9%, [N] 6.6%.

2-((3-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)propanoyl)oxy)ethyl acrylate (SP6). A dry round-bottom flask was charged with spiropyran **SP4** (1.0 g, 2.6 mmol), HEA **10** (0.34 g, 2.9 mmol), DMAP (64 mg, 0.5 mmol) and 15 mL THF. After cooling to 0°C, DCC (597 mg, 2.9 mmol) was added in one portion. The reaction mixture was stirred for additional 12 h at room temperature. After removing the solvent the crude product was dissolved in DCM and washed with brine. Recrystallization from EtOAc/Hx allowed the isolation of product **SP6** (0.71 g, 1.5 mmol, 57%) as yellow crystals.
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.08 – 7.88 (m, 2H, H5, H7), 7.20 (dd, *J* = 7.7, 7.5 Hz, 1H, H6'), 7.10 (d, *J* = 7.3 Hz, 1H, H4'), 6.96 – 6.86 (m, 2H, H4, H5'), 6.73 (d, *J* = 9.1 Hz, 1H, H8), 6.62 (d, *J* = 7.7 Hz, 1H, H7'), 6.40 (d, *J* = 17.3 Hz, 1H, CI=**CH$_2$**), 6.09 (dd, *J* = 17.3, 10.5 Hz, 1H, CI-**H**), 5.86 (d, *J* = 10.6 Hz, 1H, H3), 5.84 (d, *J* = 10.5 Hz, 1H, CI=**CH$_2$**) 4.36 – 4.20 (m, 4H, HE, HF), 3.74 – 3.44 (m, 2H, HA), 2.81 – 2.55 (m, 2H, HB), 1.26 (s, 3H, C3'-**Me$_2$**), 1.14 (s, 3H, C3'-**Me$_2$**).
^{13}C-NMR (101 MHz, $CDCl_3$) δ: 171.54 (CC), 165.76 (CH), 159.33 (C8a), 146.16 (C7a'), 141.04 (C6), 135.92 (C3a'), 131.45 (CI=**CH$_2$**), 128.32 (C4), 127.80 (2C, C6' and CI), 125.84 (C7), 122.71 (C5), 121.87 (2C, C3 and C4'), 119.83 (C5'), 118.56 (C4a), 115.49 (C8), 106.72 (C7), 106.66 (C2), 62.12 (2C, CE and CF), 52.88 (C3'), 39.12 (CA), 33.39 (CB), 25.70 (C3'-**Me$_2$**), 19.71 (C3'-**Me$_2$**).
IR (cm^{-1}): 2930, 2116, 1726, 1480, 1332, 1269, 1165, 948, 746.
UV/VIS (MeCN): ε_{366} = 1110 M^{-1}cm^{-1} $\lambda_{max,UV}$ = 568 nm
LRMS-ESI$_{pos}$ (*m/z*): $[MH]^+$ calc. for $C_{26}H_{27}N_2O_7$ 479.2; found 478.9
EA: calc. [C] 65.3%, [H] 5.5%, [N] 5.9%; found [C] 65.6%, [H] 5.6%, [N] 6.1%.

Synthesis of methacrylate functionalized spirooxazines



1-nitrosonaphthalene-2,7-diol (12). A round-bottom flask was charged with diol **11** (4.0 g, 25 mmol) suspended in 0.6 M aqueous NaOH (43 mL). After cooling to 0°C, $NaNO_2$ (1.73 g, 25 mmol) was added in one portion. The reaction mixture was then acidified with concentrated H_2SO_4 (3.0 mL) and stirred for 1 h at 0°C. The precipitated material was isolated and washed with 0.1 M aqueous HCl followed by water to obtain nitroso-compound **12** (4.8 g, 25 mmol, 99%) as a dark brown solid.
^{1}H-NMR (400 MHz, d_6-DMSO) δ: 10.25 (s, 1H, OH), 8.47 (s, 1H, OH), 7.61 (s, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.18 (s, 1H).
^{13}C-NMR (101 MHz, d_6-DMSO) δ: 159.93, 155.62, 136.33, 132.05, 129.09, 124.03, 123.39, 117.16, 115.22, 107.20.
IR (cm^{-1}): 3149, 1524, 1199, 1224, 1023, 827.
LRMS-ESI$_{pos}$ (*m/z*): $[MH]^+$ calc. for $C_{10}H_8NO_3$ 190.0; found 190.0

1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazin]-9'-ol (SO1). Nitroso-compound **12** (3 g, 15.9 mmol) was dissolved in 32 mL EtOH. The mixture was heated to 78°C and a premixed solution of indoline **13** (4.76 g, 15.8 mmol) and NEt_3 (4.4 mL, 31.7 mmol) in 20 mL EtOH was added drop-wise. After refluxing for 2 h, the solvent was removed. Recrystallization from EtOH resulted in spirooxazine **SO1** (5.6 g, 12.6 mmol, 79%) as a light brown powder.
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 10.04 (s, 1H, OH), 7.90 (d, *J* = 2.5 Hz, 1H, H5), 7.69 (s, 1H, H3), 7.63 (d, *J* = 8.8 Hz, 1H, H8), 7.56 (d, *J* = 8.8 Hz, 1H, H9), 7.21 (dd, *J* = 7.7, 7.0 Hz, 1H, H6'), 7.07 (m, 2H, H7, H4'), 6.89 (dd, *J* = 7.2, 7.0 Hz, 1H, H5'), 6.82 (d, *J* = 8.8 Hz, 1H, H10), 6.56 (d, *J* = 7.7 Hz, 1H, H7'), 2.75 (s, 3H, N-Me), 1.34 (s, 6H, C3'-**Me$_2$**).
^{13}C-NMR (101 MHz, $CDCl_3$) δ: 155.23 (C6), 150.29 (C3), 147.51 (C7a'), 144.87 (C10a), 135.79 (C3a'), 132.35 (C4b), 130.14 (C8), 129.86 (C9), 127.94 (C6'), 124.56 (C8a), 121.88 (C4a), 121.42 (C4'), 119.76 (C5'), 115.94 (C7), 114.00 (C10), 107.06 (C7'), 103.69 (C5), 98.53 (C2), 51.71 (C3'), 29.58 (N-Me), 25.38 (C3'-**Me$_2$**), 20.73(C3'-**Me$_2$**).
IR (cm^{-1}): 3309, 2968, 2361, 1630, 1448, 1081, 965, 829, 737.
UV/VIS (MeCN): ε_{366} = 1990 M^{-1}cm^{-1} $\lambda_{max,UV}$ = 575 nm
LRMS-ESI$_{pos}$ (*m/z*): $[MH]^+$ calc. for $C_{22}H_{21}N_2O_2$ 345.2; found 345.2

1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazin]-9'-yl methacrylate (SO2). A dry round-bottom flask was charged with spirooxazine **SO1** (250 mg, 0.73 mmol), NEt_3 (160 µL, 1.1 mmol) and 3.0 mL DCM. After cooling to 0°C, methacryloyl chloride **5** (150 µL, 1.4 mmol) was added drop-wise. The mixture was stirred for 18 h at room temperature. The reaction was quenched with 1 M HCl solution and extracted with DCM. The organic layers were combined and washed with brine and dried over Na_2SO_4. Product **SO2** was then purified by preparative TLC. Methacrylate **SO2** (0.33 mmol, 45%) was isolated as an off-white powder.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.29 (d, *J* = 2.4 Hz, 1H, H5), 7.77 (d, *J* = 8.8 Hz, 1H, H8), 7.72 (s, 1H, H3), 7.66 (d, *J* = 8.9 Hz, 1H, H9), 7.24 – 7.18 (m, 2H, H7, H6'), 7.09 (d, *J* = 8.2 Hz, 1H, H4'), 7.00 (d, *J* = 8.9 Hz, 1H, H10), 6.91 (dd, *J* = 7.4 Hz, 1H, H5'), 6.59 (d, *J* = 7.7 Hz, 1H, H7'), 6.42 (s, 1H, -O(CO)C=**CH$_2$**Me), 5.80 (s, 1H, -O(CO)C=**CH$_2$**Me), 2.77 (s, 3H, N-Me), 2.12 (s, 3H, -O(CO)C=CH_2**Me**), 1.36 (s, 6H, C3'-**Me$_2$**).
^{13}C-NMR (101 MHz, $CDCl_3$) δ: 166.08 (-O(**C**O)R), 150.78 (C3), 149.99 (C7a'), 147.54 (C10a), 144.73 (C6), 135.94 (2C, C3a' and -O(CO)**C**=CH_2Me), 131.76 (C4b), 129.99 (C9), 129.28 (C8), 128.00 (C6'), 127.25 (2C, C8a and -O(CO)C=**CH$_2$**Me), 122.86 (C4a), 121.47 (C4'), 119.86 (C5'), 119.38 (C7), 116.53 (C10), 112.95 (C5), 107.11 (C7'), 98.75 (C2), 51.84 (C3'), 29.59 (N-Me), 25.37 (C3'-**Me$_2$**), 20.74 (C3'-**Me$_2$**), 18.42 (-O(CO)C=CH_2**Me**).
IR (cm^{-1}): 2971, 2360, 1728, 1121, 740.
UV/VIS (MeCN): ε_{366} = 1764 $M^{-1}cm^{-1}$ $\lambda_{max,UV}$ = 580 nm
LRMS-ESI$_{pos}$ (*m/z*): $[MH]^+$ calc. for $C_{26}H_{25}N_2O_3$ 413.2; found 413.4
EA: calc. [C] 75.7%, [H] 5.9%, [N] 6.8%; found [C] 74.9%, [H] 6.0%, [N] 6.5%.

XPS Data

Table S1 XPS-measurements of postmodified PC membranes. For comparison, XPS-values before post-modification are shown in italic. All results shown in At.-%.

Sample	C 1s	O 1s	N 1s
PC (calc.)	*84.2*	*15.8*	*0.0*
PC-PHEMA-**SP4**	84.0	16.0	0.0
PHEMA	83.8	16.2	0.0
PC-PHEA-**SP4**	83.2	16.8	0.0
PHEA	82.5	17.5	0.0
PC-PAEMA-**SP4**	80.4	16.6	3.0
PAEMA	73.9	19.9	6.2

Table S2 XPS-measurements of different coated PC-membranes. All membranes are modified in a copolymerization process. All results shown in At.-%.

Sample	C 1s	O 1s	N 1s
PC (calc.)	*84.2*	*15.8*	*0*
PHEMA; **SP2**	81.7	18.3	0
PHEMA; **SP5**	75.3	24.7	0
PHEMA (calc.)	*66.6*	*33.3*	*0*
PHEA; **SP3**	84.2	15.8	0
PHEA; **SP6**	82.7	17.3	0
PHEA (calc.)	*62.5*	*37.5*	*0*
PAEMA; **SP2**	76.8	21.2	2.0
PAEMA (calc.)	*66.7*	*22.2*	*11.1*
PMMA; **SP2**	80.0	20.0	0
PMMA (calc.)	*71.4*	*28.6*	*0*

Angle-dependent XPS measurements

On all investigated positions, signals from both metallic and oxide Si (SiO_2) originating from the substrate could be detected. This indicates that the total polymer thicknesses after the coating process are smaller than 10 nm (Table 2) on these positions assuming that no holes are present in the coating.

Table S3. *Normalized At.-% (all detected elements) for PC and PHEMA.*

Sample	Meas. Emission Angle	C	O	Si
PC-PHEMA 20°	20	56.9	28.4	14.7
PC-PHEMA 45°	45	53.0	27.2	19.8
PC-PHEMA 70°	70	53.3	24.5	22.2

Measurements at low and high emission angle to discern between top surface and bulk of the film/sample show as expected an increase in Si at higher emission angle. The C1s detail spectrum is only changing in a marginal way. A small increase in the C-O component at the lowest emission angle can be detected indicating that indeed alcohol groups of the PHEMA are slightly surface enriched. The effect is small and due to the total layer thickness (about 10 nm), the high intensity of the PC signals (shakeup peak and C 1s D at 291.1 eV) indicates a very thin PHEMA layer (1-2 nm).

The PHEMA coating on PC-coated Si wafers act as model systems for the coated membranes discussed in the paper. Because of that, a more exact determination of the film thickness in the sub-nanometer scale of the complex structured sample (4 layers Si/SiO_2/PC/PHEMA) could not be used as thickness information for the membrane coating.

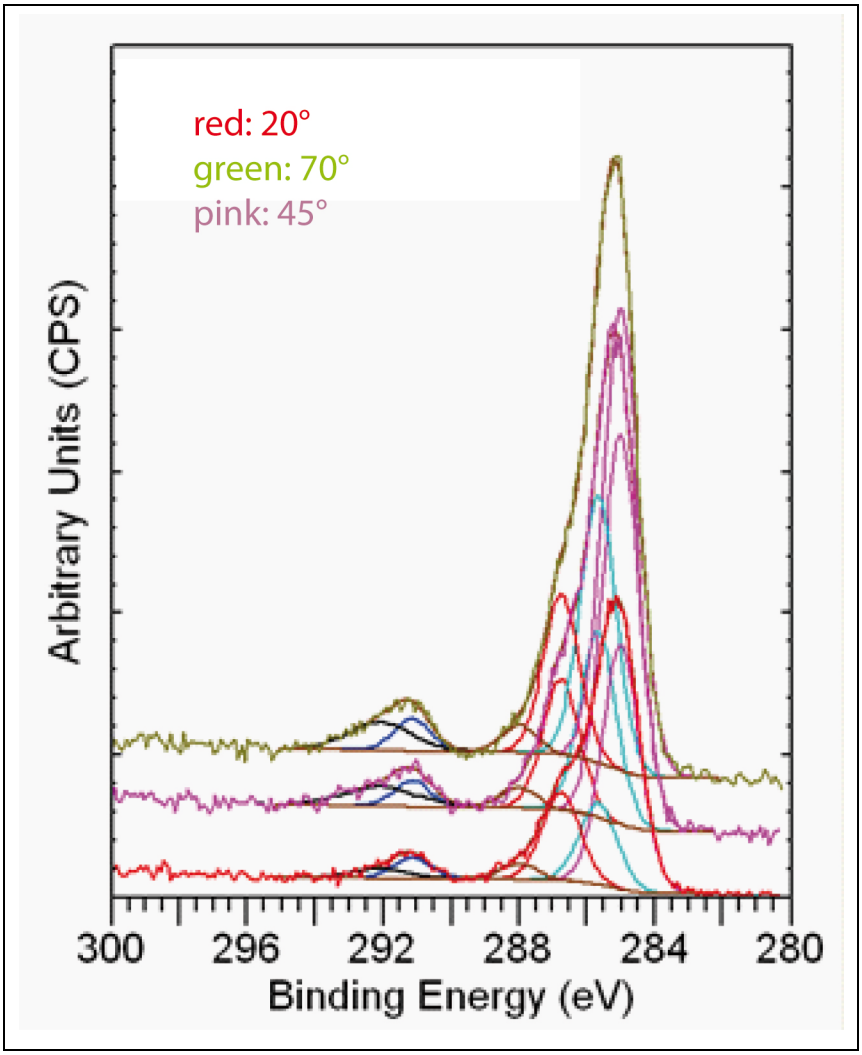


Fig. S1. *Detail spectrum of C 1s for the PC-PHEMA sample at three different emission angles (20° most surface sensitive, 45° and 70° (most bulk sensitive)).*