

Single Wavelength Colour Tuning of Spiropyran and Dthienylethene based Photochromic Coatings

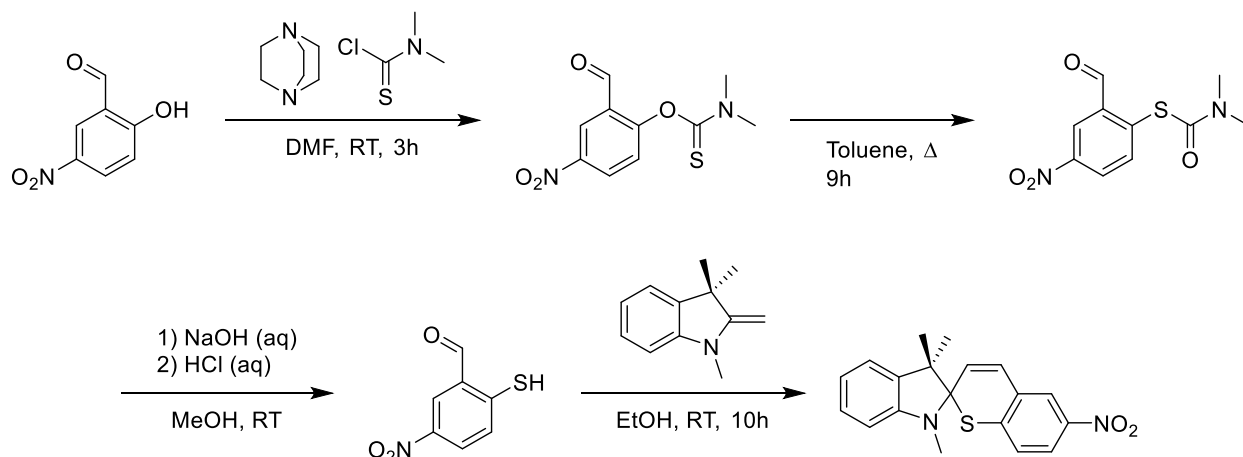
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Supporting information

S1 Synthesis and characterization of TSP

Synthesis of O-(2-formyl-4-nitrophenyl) dimethylcarbamothioate 1.

2-hydroxy-5-nitrobenzaldehyde (1.33 g, 7.97 mmol), dimethylcarbamothioic chloride (1.49 g, 12.03 mmol) and 1,4-diazabicyclo[2.2.2]octane (2.03 g, 18.11 mmol) were dissolved in dimethylformamide (54 mL). The mixture was allowed to react for 3 h where after the solids were filtered off and the crude product was concentrated in vacuo. Brine was added and the product was extracted with ethyl acetate and subsequently washed with water and brine. The organic layer was dried over Na_2SO_4 and the product was obtained by concentration in vacuo. The product obtained contained dimethylformamide determined by ^1H NMR. ^1H NMR (400 MHz, CDCl_3) δ 10.09 (s, 1H), 8.76 (d, $J = 2.8$ Hz, 1H), 8.46 (dd, $J = 8.9, 2.8$ Hz, 1H), 7.33 (d, $J = 8.9$ Hz, 1H), 3.48 (s, 3H), 3.45 (s, 3H).



Scheme 1 Synthetic route towards TSP

Synthesis of S-(2-formyl-4-nitrophenyl) dimethylcarbamothioate 2.

O-(2-formyl-4-nitrophenyl) dimethylcarbamothioate in the mixture from step 1 was dissolved in toluene (350 mL) and was allowed to reflux for 15 h. The crude product was obtained by concentration in vacuo. The crude mixture contained the desired product determined by ^1H NMR. ^1H NMR spectroscopy (400 MHz, CDCl_3) δ 10.28 (s, 1H), 8.82 (d, $J = 2.6$ Hz, 1H), 8.37 (dd, $J = 8.5, 2.6$ Hz, 1H), 7.78 (d, $J = 8.5$ Hz, 1H), 3.19 (s, 3H), 3.05 (s, 3H).

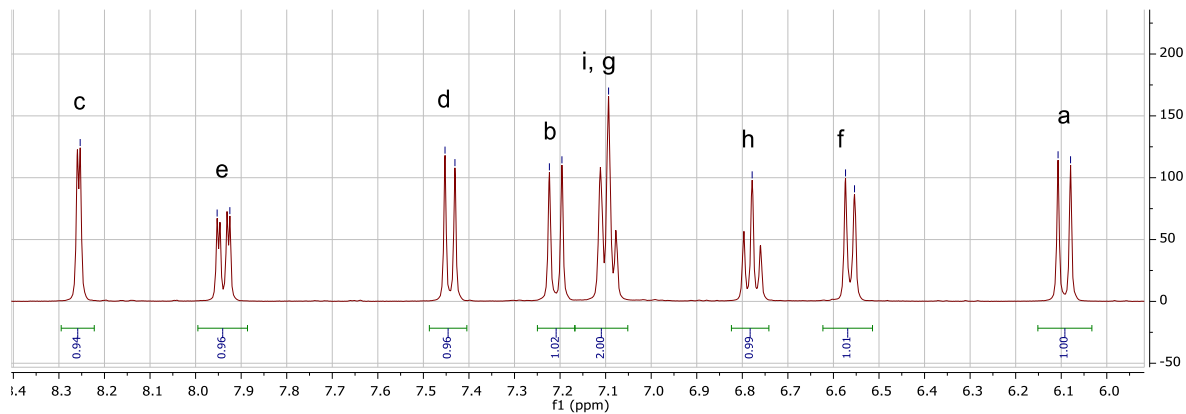
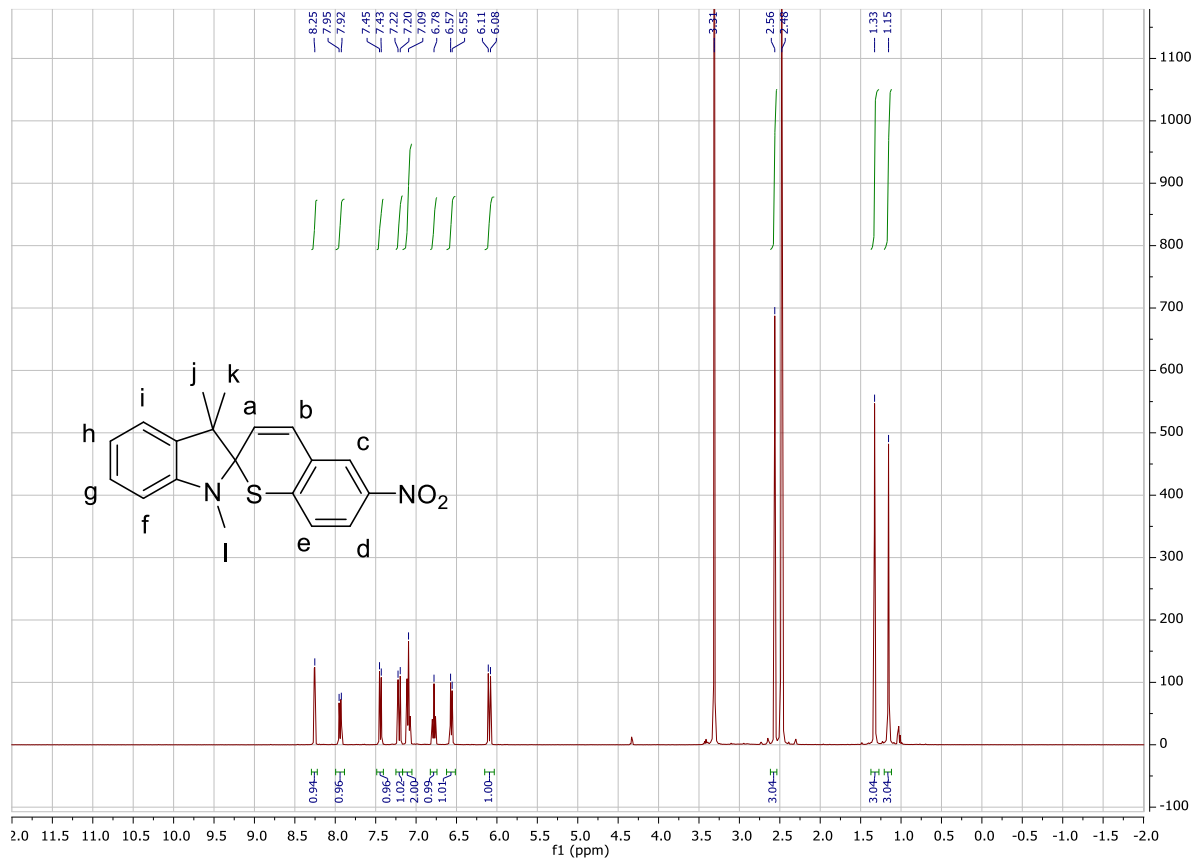
Synthesis of 2-mercapto-5-nitrobenzaldehyde 3.

The crude mixture of step 2 was dissolved in methanol (256 mL) and cooled to 0 °C. The mixture turned red upon slow addition of NaOH (0.7 M, 75 mL). The mixture reacted at room temperature for 30 min after which quenching with HCl (1.0 M, 83 mL) at 0 °C resulted in a colourless mixture. After concentration and addition of brine the product was extracted with ethyl acetate and dried over Na_2SO_4 . After concentration in vacuo, a powder was obtained (2.55 g). ^1H NMR spectroscopy (400 MHz, CDCl_3) δ 10.29 (s, 1H), 8.83 (d, $J = 2.5$ Hz, 1H), 8.38 (dd, $J = 8.5, 2.7$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 1H).

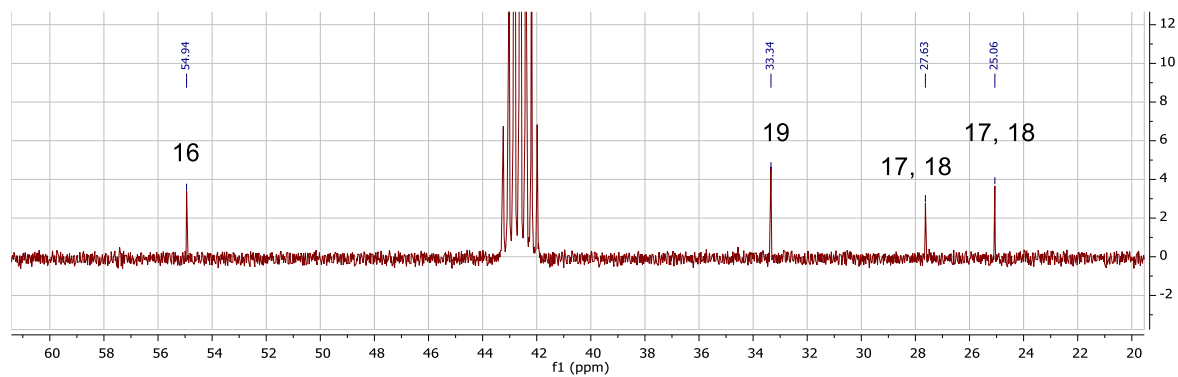
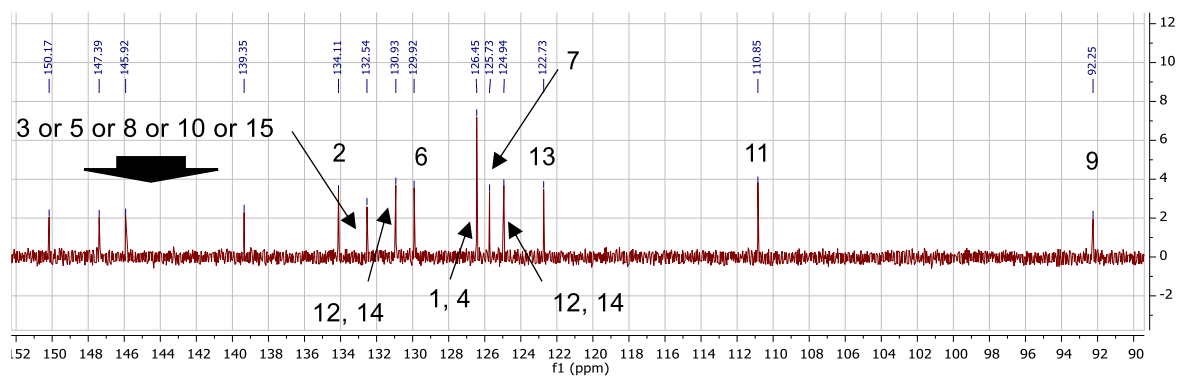
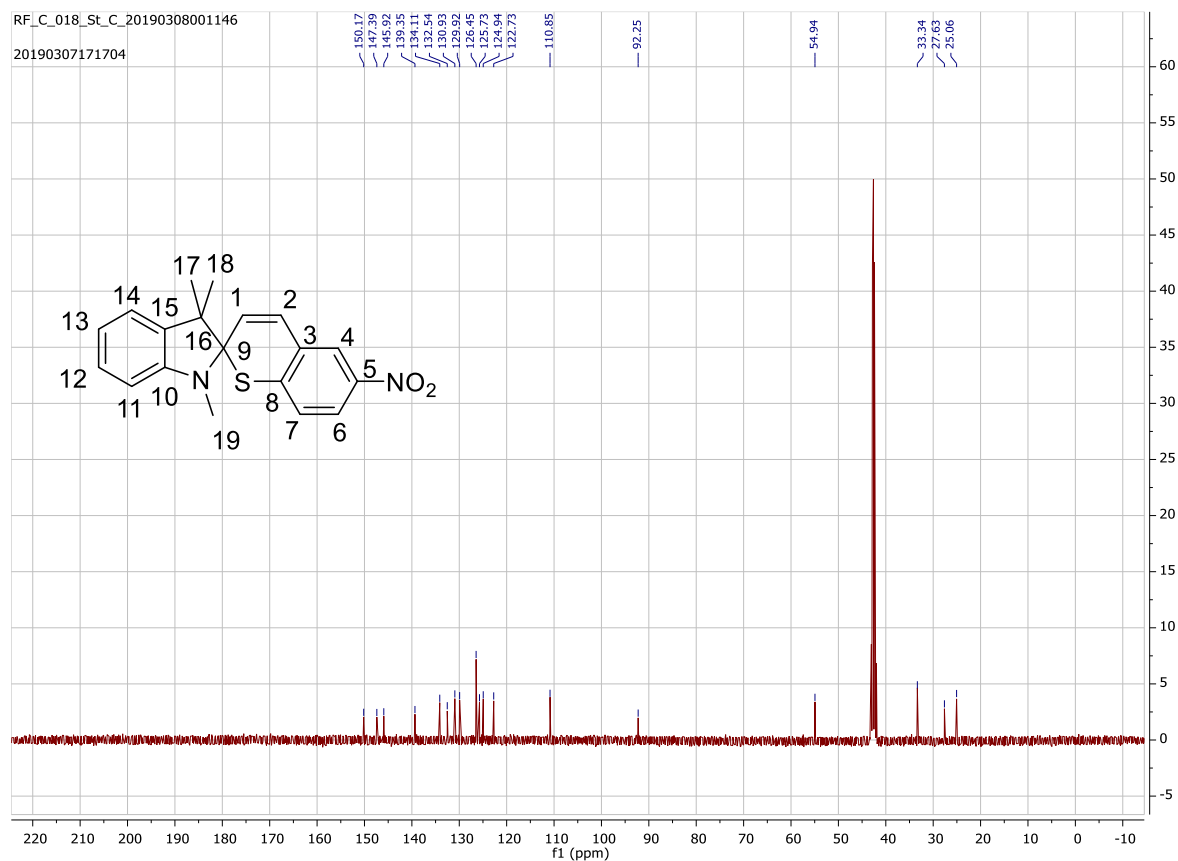
Synthesis of (R)-1,3,3-trimethyl-6'-nitrospiro[indoline-2,2'-thiochromene] 4.

The crude product of step 3 and 1,3,3-trimethyl-2-methyleneindoline (1.386 g, 1 eq., 8.00 mmol) were dissolved in ethanol (150 mL). The mixture was purged with argon and heated at reflux for 10 h. The crude product was obtained by concentration in vacuo and purified by recrystallization and flash precipitation in pentane from ethyl acetate. ^1H NMR spectroscopy (400 MHz, Acetonitrile- d_3) δ 8.15 (d, $J = 2.4$ Hz, 1H), 7.95 (dd, $J = 8.7, 2.5$ Hz, 1H), 7.39 (d, $J = 8.7$ Hz, 1H), 7.20 – 7.05 (m, 3H), 6.85 (t, $J = 7.8$ Hz, 1H), 6.57 (d, $J = 7.8$ Hz, 1H), 6.12 (d, $J = 11.0$ Hz, 1H), 2.66 (s, 3H), 1.41 (s, 3H), 1.23 (s, 3H). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.25 (s, 1H), 7.94 (d, $J = 11.2$ Hz, 1H), 7.44 (d, $J = 8.7$ Hz, 1H), 7.21 (d, $J = 11.0$ Hz, 1H), 7.09 (s, 2H), 6.78 (s, 1H), 6.56 (d, $J = 7.9$ Hz, 1H), 6.09 (d, $J = 10.9$ Hz, 1H), 2.56 (s, 3H), 1.33 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 150.2, 147.4, 145.9, 139.4, 134.1, 132.5, 130.9, 129.9, 126.5, 125.7, 124.9, 122.7, 110.9, 92.3, 33.3, 27.6, 25.1. Elemental Analysis: Calc. C, 67.43; H, 5.36; N, 8.28; S, 9.47 measured. C, 66.93; H, 5.49; N, 8.04; S, 9.31.

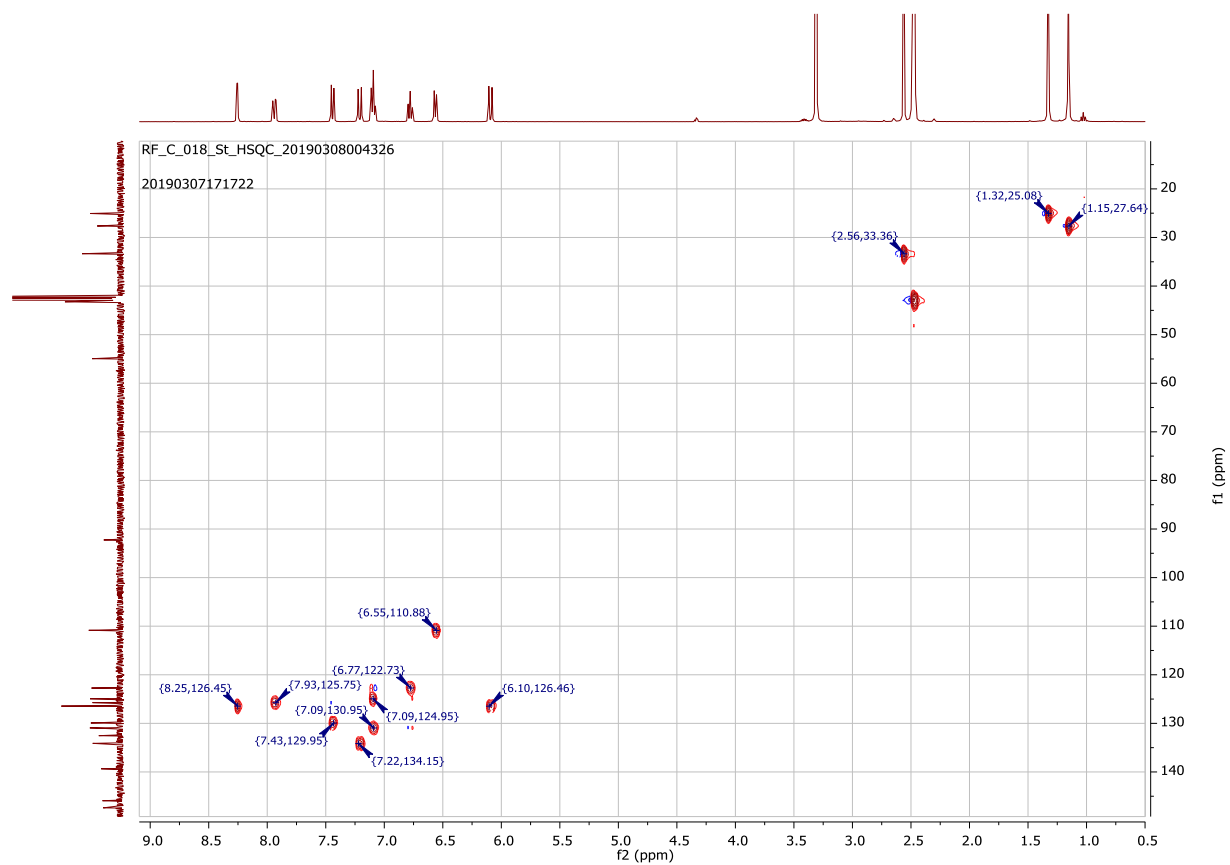
¹H-NMR

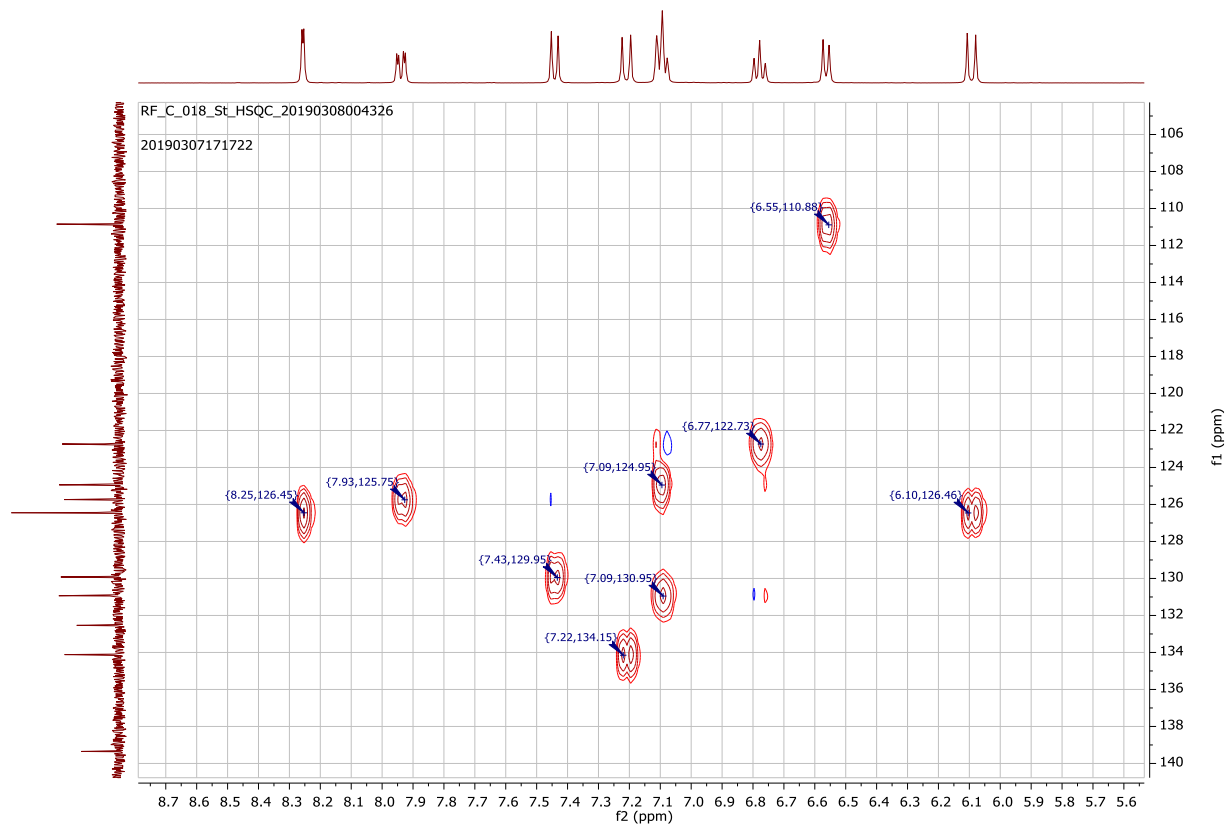


¹³C NMR spectra

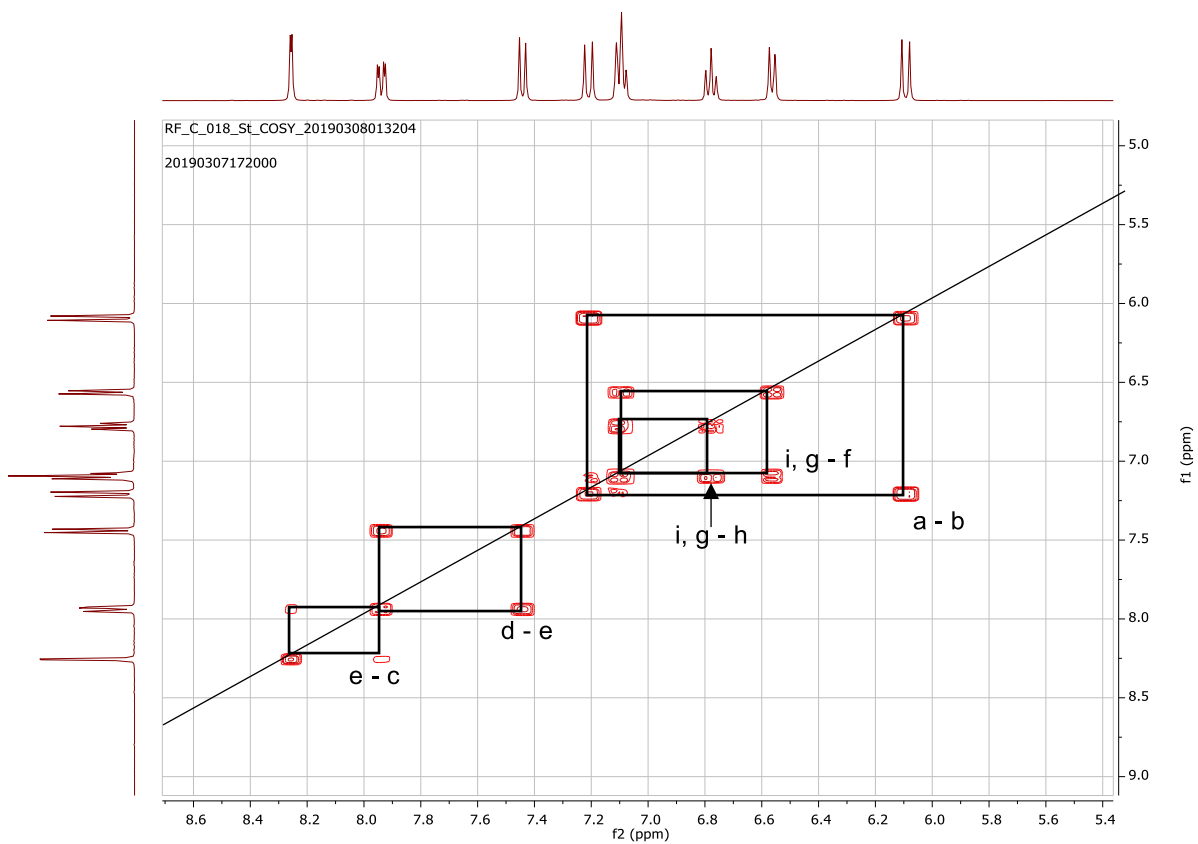


HSQC spectra

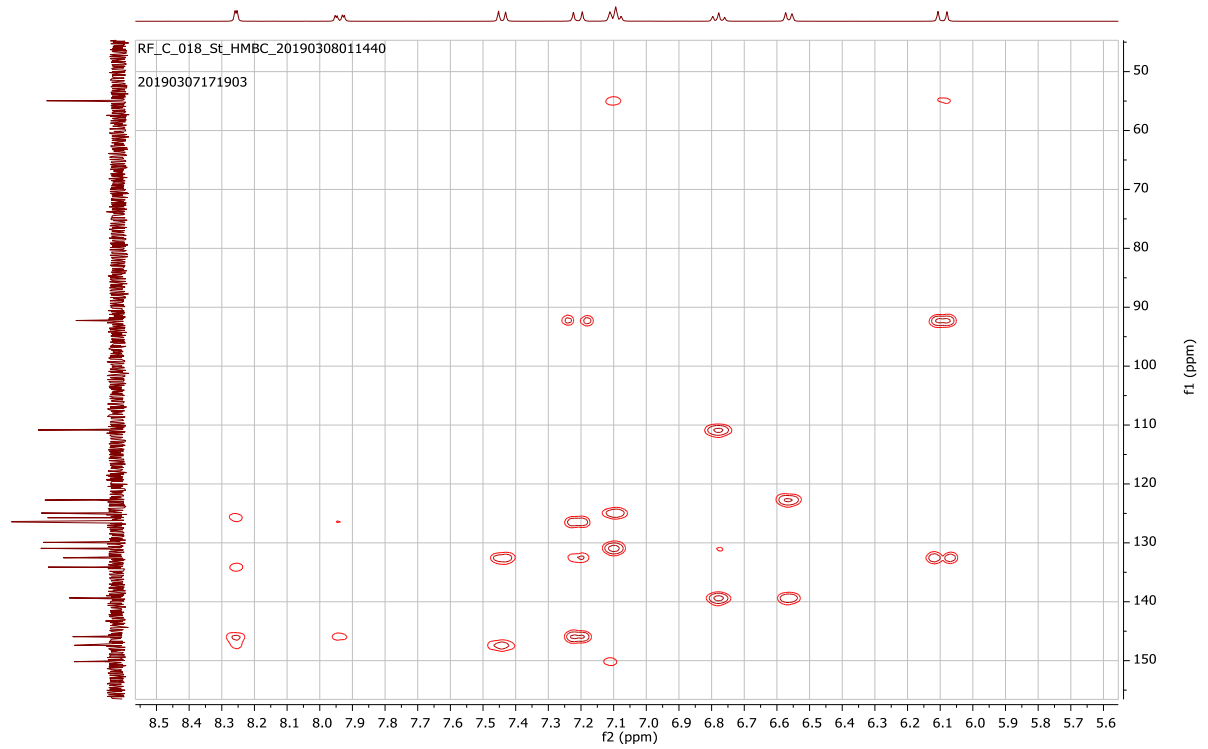
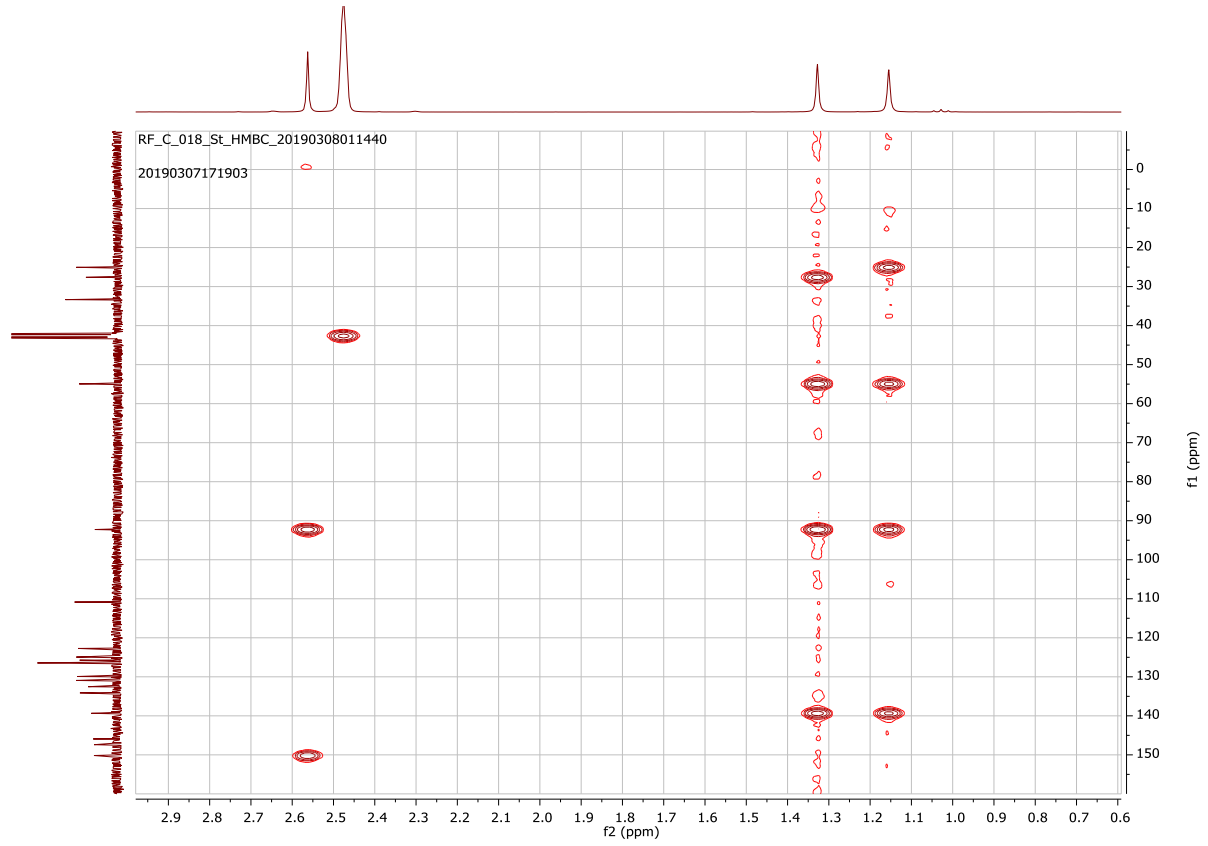




^1H - ^1H COSY spectrum



HMBC spectrum



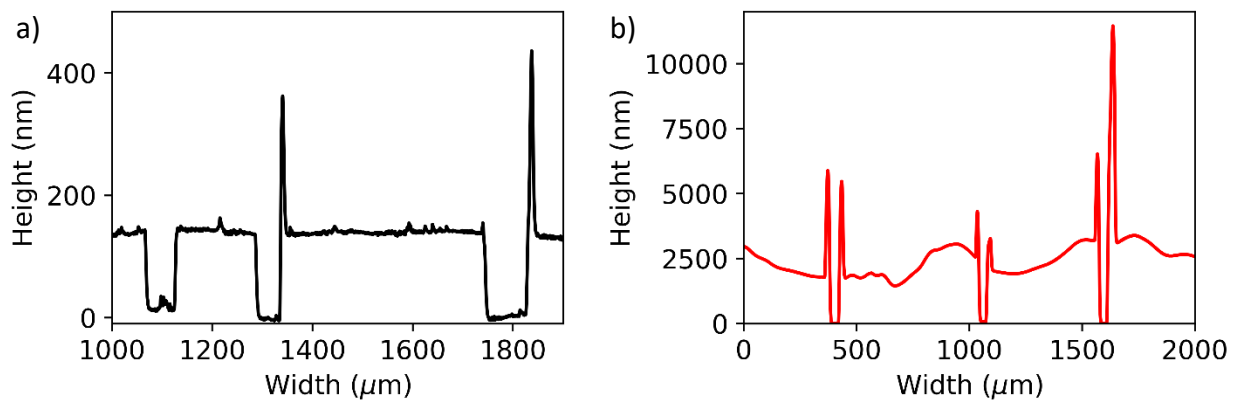


Fig. S1 Profiles determined for PMMA films prepared from solutions of PMMA in ethyl acetate at a): 2% and b): 16%.

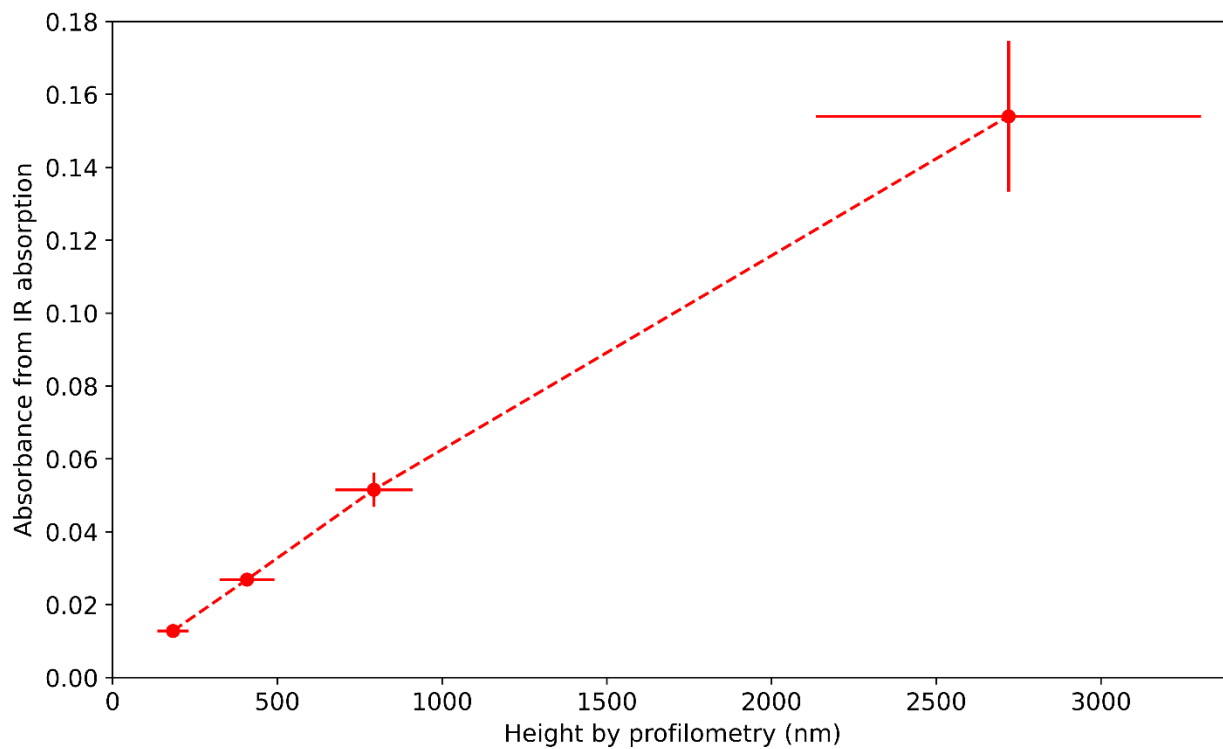


Fig. S2 Calibration curve for FTIR absorbance with thickness of films determined by profilometry

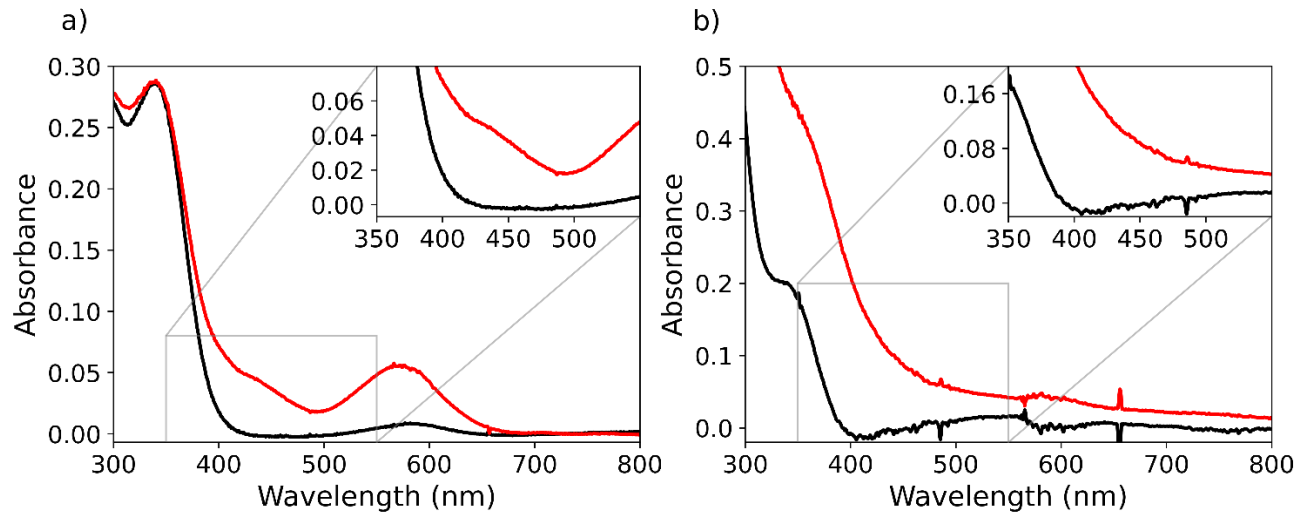


Fig. S3 UV-vis absorption spectra of **NSP-PMMA** films (black) and **NSP-PMMA** films which are subjected to acidic vapours of a) HCl vapour and b) $\text{CF}_3\text{SO}_3\text{H}$ vapour.

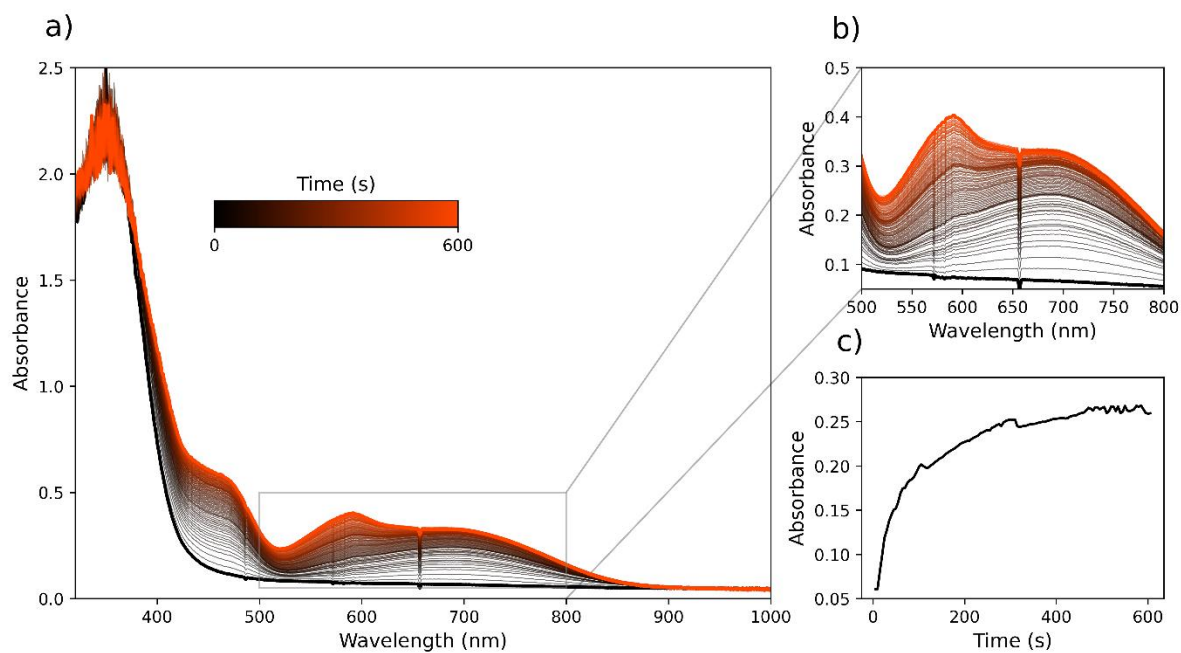
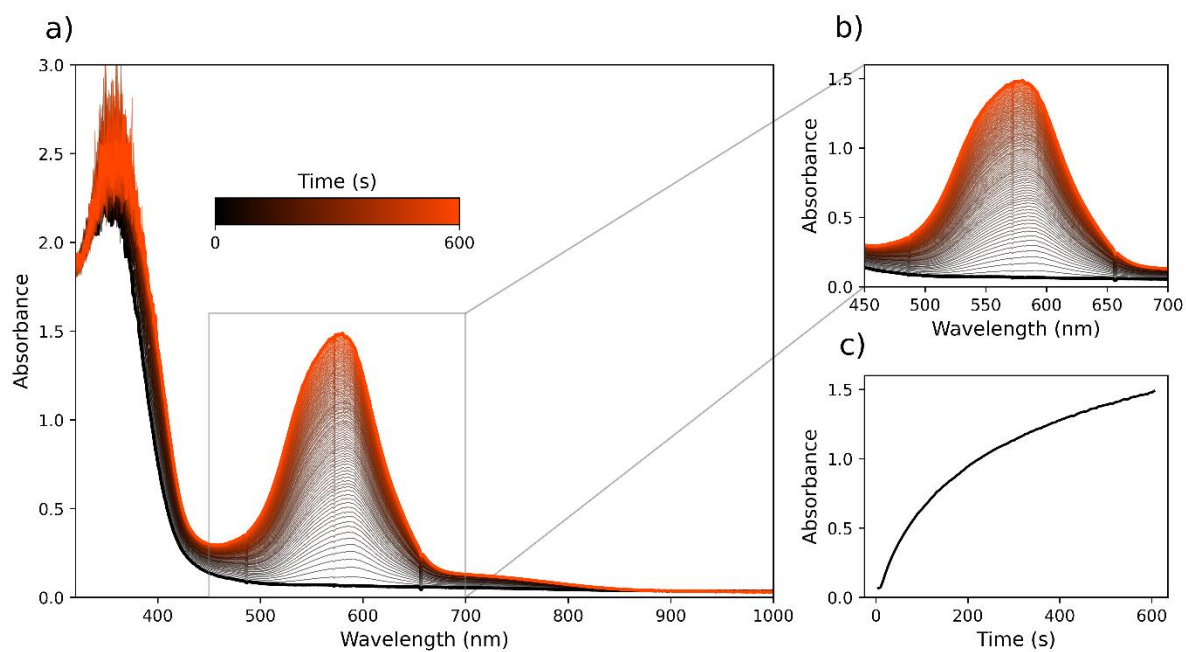


Figure S4 UV/vis absorption spectra of slides containing 6 layers of PMMA first with three layers of **TSP** and second with 3 layers of **NSP** present with intermediate layers of HEC. Irradiation from the **NSP** side results in the top figure and the **TSP** side bottom figure. With a) full UV-vis absorption spectra, b) expansion of visible absorbance and c) the trajectory towards the PSS_{365 nm}.

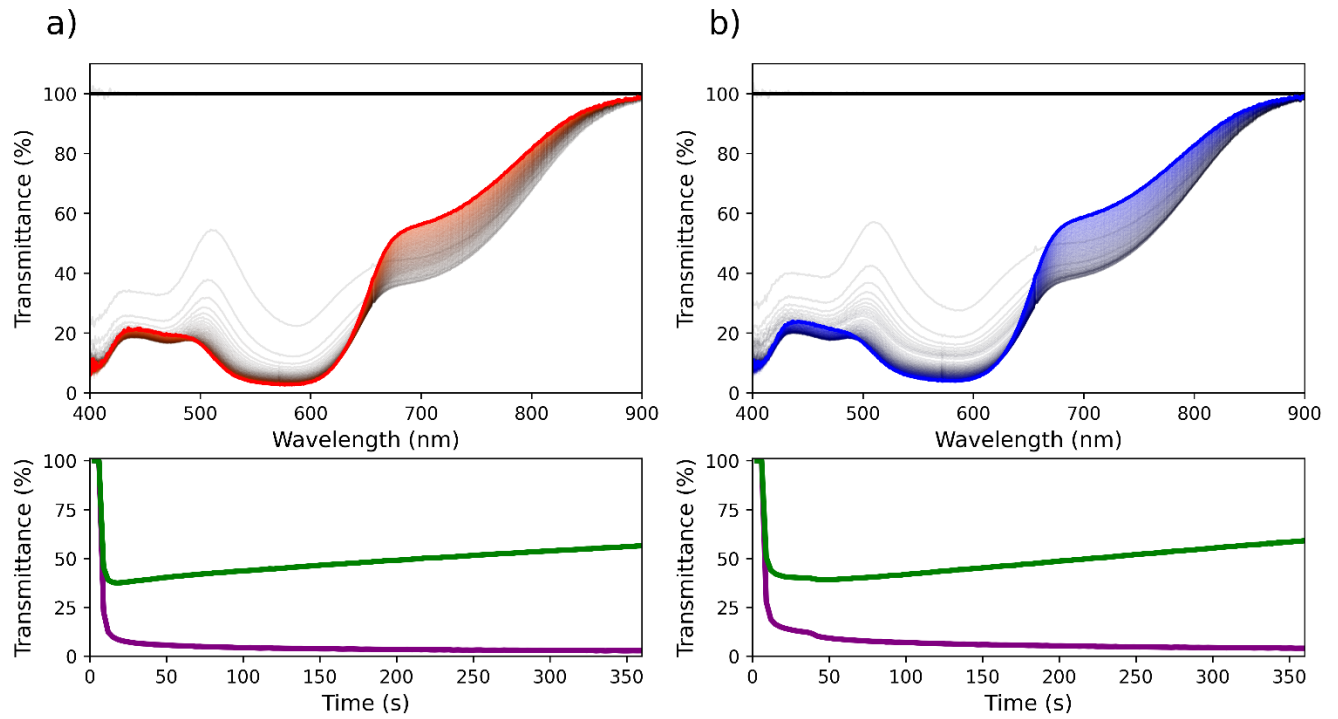


Fig. S5 UV/vis absorption spectra of slides containing 6 layers of PMMA each with **TSP** and **NSP** present with intermediate layers of HEC. Irradiation from either side (side (a) or side (b)) of the slide results in identical changes. The full UV-vis transmittance spectra are shown above and the trajectory towards the PSS₃₆₅ nm at 580 nm (purple) and 700 nm (green) below.

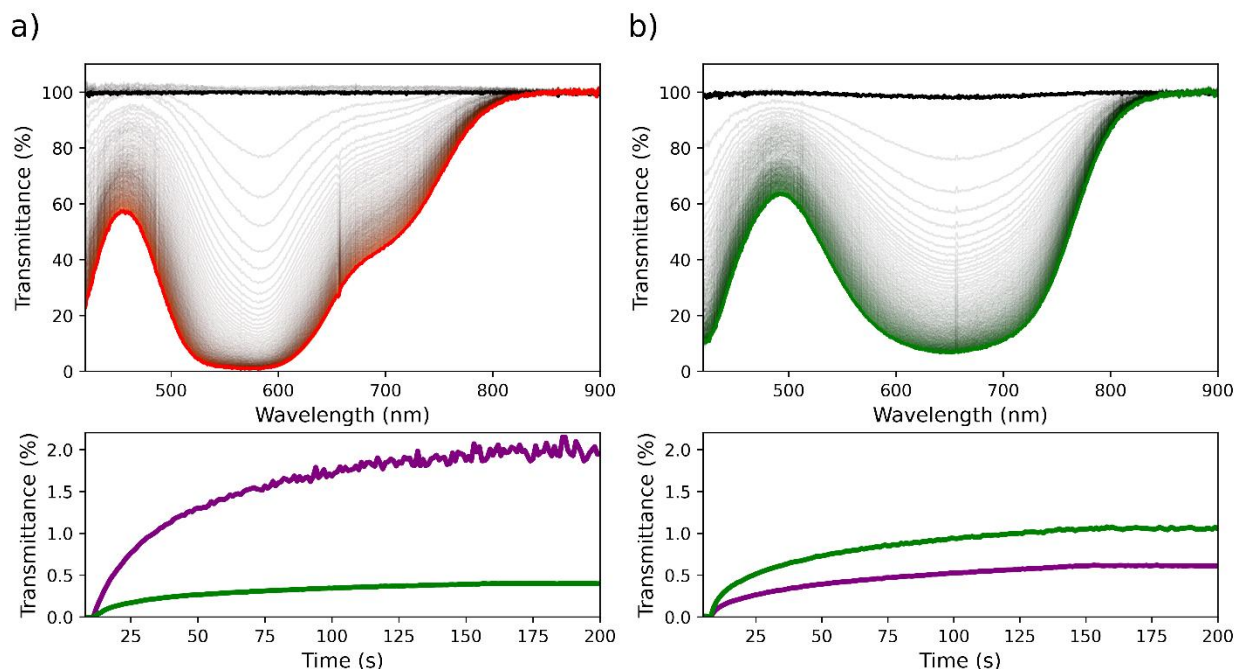


Fig. S6 UV/vis absorption spectra of slides containing 4 layers of PMMA with 3 layers containing **NSP** and one layer containing **DTE** present with intermediate layers of HEC. Irradiation from the **NSP** side (a) of the slide results in switching of the **NSP** and minor switching of **DTE** and irradiation from the **DTE** side (b) of the slide results in switching of **DTE**. The full UV-vis transmittance spectra is shown above and the trajectory towards the PSS₃₆₅ nm at 560 nm (purple) and 680 nm (green) below.

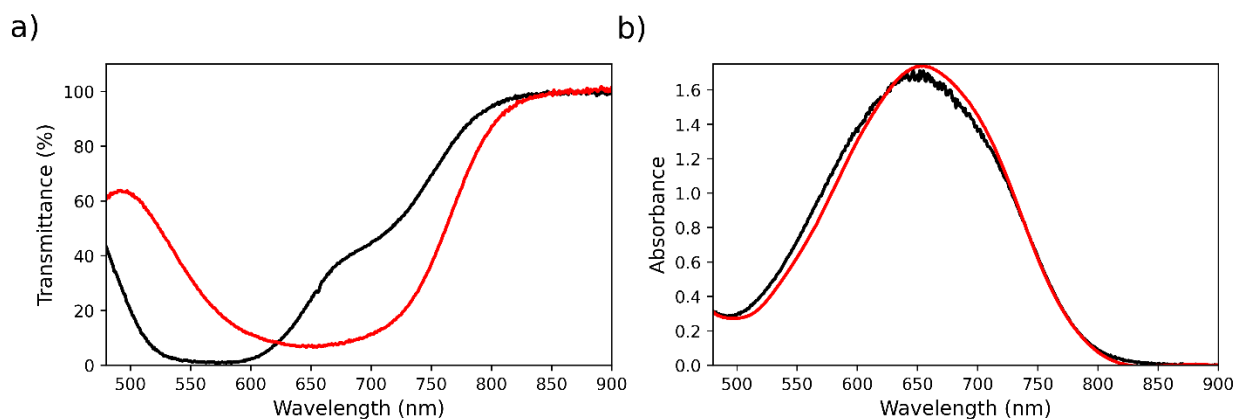


Fig. S7 (a) UV/vis transmission spectra of a multilayered slide containing 4 layers of PMMA with 3 layers containing **NSP** and one layer containing **DTE** present with intermediate layers of HEC irradiated (365 nm) from the **NSP** side (black) and a single layered PMMA slide containing **DTE** irradiated to photo stationary state (red). (b) UV/vis absorption spectra of a multilayered slide containing 4 layers of PMMA with 3 layers containing **NSP** and one layer containing **DTE** present with intermediate layers of HEC irradiated (365 nm) from the **DTE** side (black) and a normalized absorption spectrum of a single layered PMMA slide containing **DTE** irradiated to photo stationary state (red).

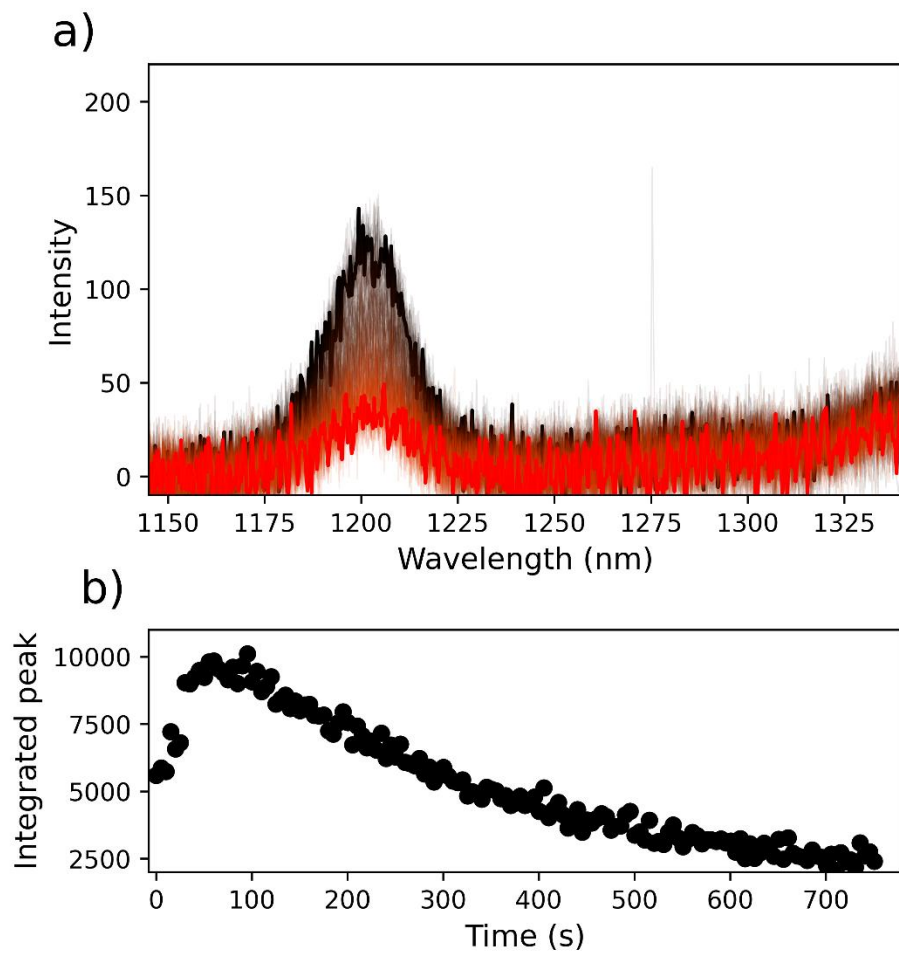


Fig. S8 (a) NIR emission spectra from a solution containing **TSP over time** under irradiation at 355 nm with a ns-Nd-YAG pulsed laser showing emission from singlet oxygen at 1270 nm increase and subsequently decrease. (b) Integrated area of the singlet oxygen emission band over time.