Supporting Information

Synthesis of 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethyl 2-azidoacetate

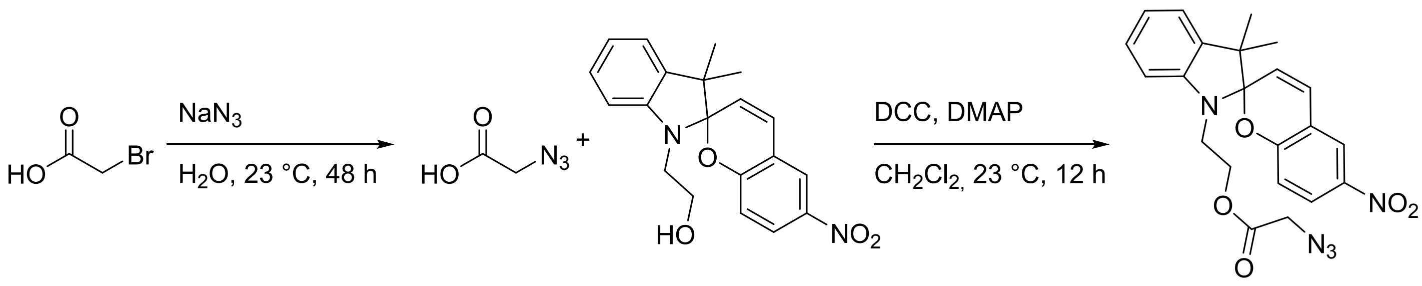
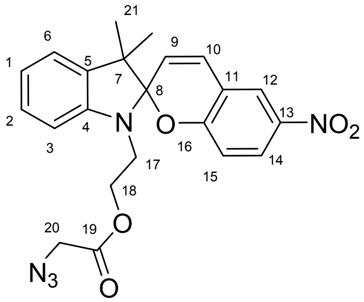


Figure SI1A: Synthesis of the azide-spiropyran (2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethyl 2-azidoacetate). 2-Azidoacetic acid was prepared following a literature procedure.[1]



2-(3',3'-Dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethyl 2-azidoacetate was prepared by the following procedure: 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran (375 mg, 1.06 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (20 mL) and heated to 35 °C until the colored merocyanine form was converted into the colorless spiropyran form. *N,N'*-Dicyclohexylcarbodiimide (275 mg, 1.33 mmol, 1.25 equiv.), 4-dimethylaminopyridine (325 mg, 2.66 mmol, 2.5 equiv.) and 2-azidoacetic acid (161 mg, 1.60 mmol, 1.5 equiv.) were added and the reaction mixture was stirred at 23 °C for 12 h. Subsequently, a saturated sodium carbonate solution (20 mL) was added, the aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL) and the combined organic phases were dried over Na_2SO_4. After removing the solvent *in vacuo* the crude product was purified by fast column chromatography (SiO_2, *i*Hex/EtOAc = 8/2) (the spiropyran form is converted rapidly into the merocyanine form on the column, which sticks on the SiO_2) and further by crystallization from *n*heptane/CH_2Cl_2. The title compound was isolated as pale-yellow crystals (365 mg, 0.84 mmol, 79 %).

HR-MS (EI) for $C_{22}H_{21}N_5O_5^{\cdot+}$, $[M]^{\cdot+}$, calcd. 435.1537, found 435.1536.

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 8.05 – 7.99 (m, 2H, H-C(12), H-C(14)), 7.21 (td, J = 7.7, 1.3 Hz, 1H, H-C(2)), 7.10 (dd, J = 7.4, 1.3 Hz, 1H, H-C(6)), 6.95 – 6.88 (m, 2H, H-C(1), H-C(10)), 6.76 (d, *J* = 8.8 Hz, 1H, H-C(15)), 6.67 (dd, *J* = 7.7 Hz, 1H, H-C(3)), 5.89 (d, *J* = 10.4 Hz, 1H, H-C(9)), 4.40 (dt, *J* = 11.2, 6.4 Hz, 1H, H-C(18)), 4.32 (dt, *J* = 11.1, 6.2 Hz, 1H, H-C(18)), 3.86 – 3.75 (m, 2H, H-C(20)), 3.60 – 3.51 (m, 1H, H-C(17)), 3.51 – 3.44 (m, 1H, H-C(17)), 1.28 (s, 3H, H-C(21)), 1.17 (s, 3H, H-C(21)).

^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 168.3 (C(19)), 159.4 (C(16)), 146.6 (C(4)), 141.3 (C(13)), 135.8 (C(5)), 128.6 (C(10)), 128.0 (C(2)), 126.2 (C(14)), 123.0 (C(18)), 122.1 (C(6)), 121.7 (C(9)), 120.3 (C(1)), 118.5 (C(11)), 115.7 (C(15)), 106.7 (C(3)), 106.7 (C(8)), 63.9 (C(18)), 53.0 (C(7)), 50.4 (C(20)), 42.4 (C(17)), 26.0 (C(21)), 20.0(C(21)).

IR: □/cm^{-1} = 2101 (m), 1742 (m), 1651 (w), 1608 (w), 1575 (w), 1507 (m), 1478 (m), 1456 (m), 1445 (w), 1334 (s), 1273 (s), 1228 (m), 1195 (m), 1179 (m), 1157 (m), 1122 (m), 1088 (s), 1012 (m), 949 (s), 919 (s), 836 (w), 806 (s), 748 (vs), 685 (w).

Melting point: 106 °C.

R_f (SiO_2, hexanes:EtOAc = 8:2) = 0.42.

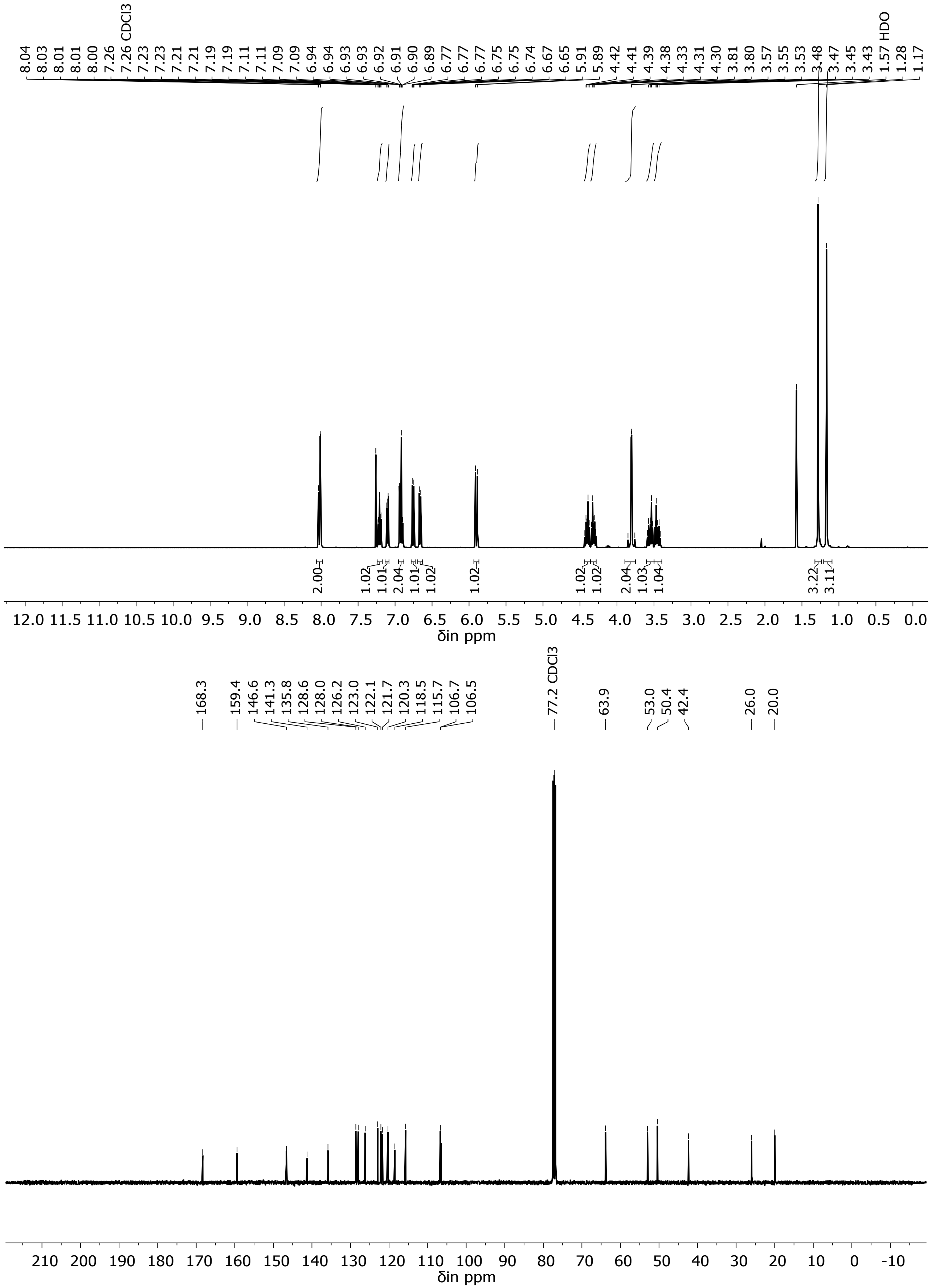


Figure SI1B: 400 MHz ^{1}H-NMR Spectrum (top) and 100 MHz ^{13}C-NMR Spectrum (bottom) of 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethyl 2-azidoacetate in CDCl$_3$.

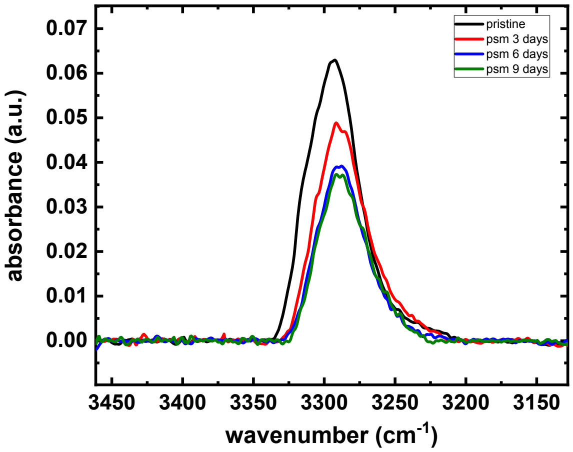


Fig. SI2: Infrared spectra of the Cu_2(e-BPDC)$_2$(dabco) during PSM. The band at 3300 cm^{-1} is correlated to C-H vibrational band of ethynyl. The decrease this band results from the ethynyl-azide reaction, resulting in the anchoring of the photoswitchable spiropyran azide. The maximum yield of 41.5% is obtained after 9 days.

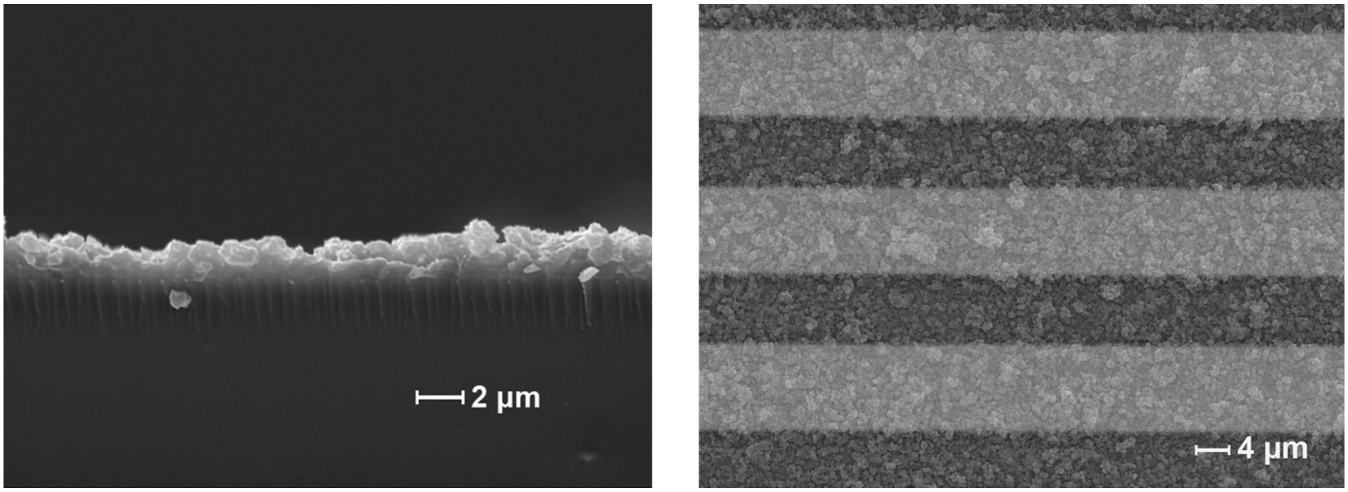


Fig. SI3: Scanning Electron Microscopy (SEM) pictures of the sample. Left: Side-view of the broken sample shows the cross section. A sample thickness of 0.7 µm was estimated. Right: Top-view of the SURMOF sample on the interdigitated gold electrodes. The gold electrodes are visible as bright stripes. The homogeneous SURMOF coverage of the substrate is visible.

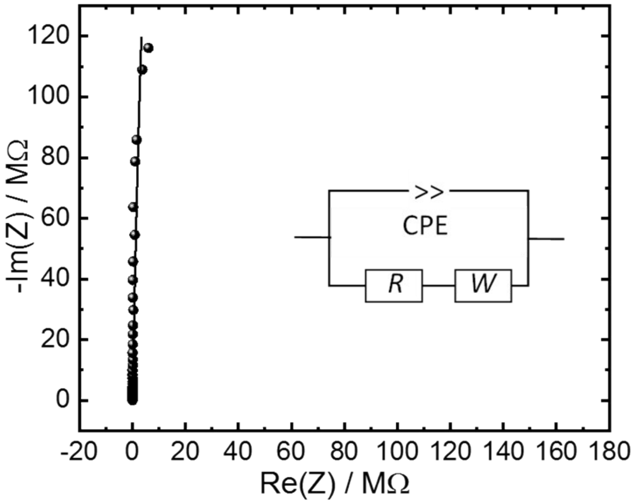


Fig. SI4: Impedance Nyquist plot of the empty $Cu_2(SP\text{-}BPDC)_2(dabco)$ SURMOF. The thin line represents the fit with the reference circuit, showing an ohmic resistance of approximately 1.4 10^{13} Ω. This means the empty SURMOF sample shows essentially no conductivity.

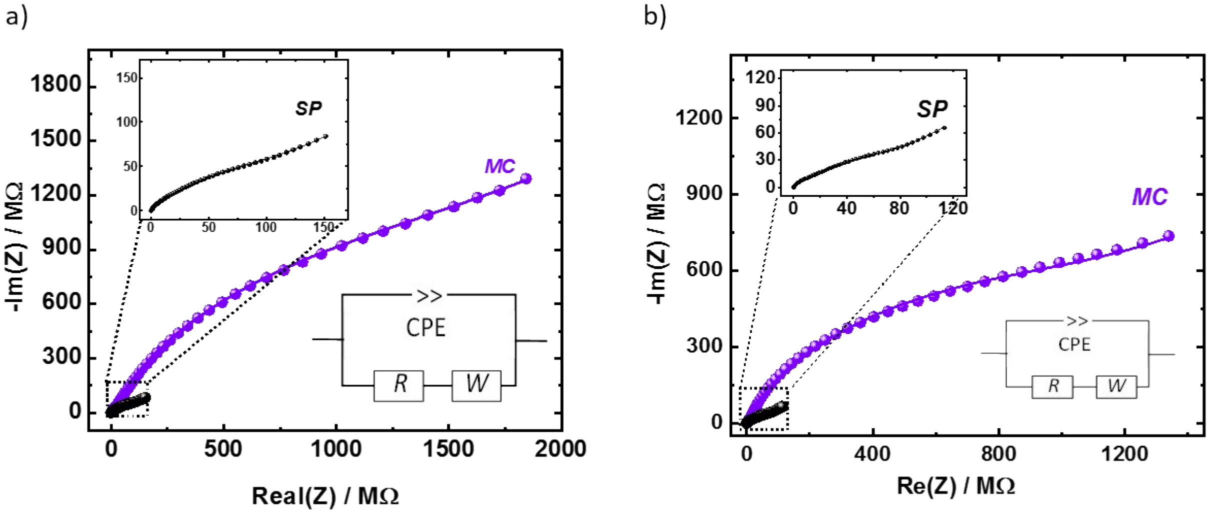


Figure SI5: a) Nyquist plot of impedance *Z* of ethanol (a) and methanol (b) in Cu_2(SP-BPDC)$_2$(dabco). The black data are measured in the spiropyran form, violet after irradiating the sample with 365nm UV light resulting in merocyanine form. The dotted lines are the fits to the experimental data based on the reference circuit. The ohmic resistances of ethanol@SURMOF were determined to be 131 MΩ (black) and 2343 MΩ (violet) as well as 84 MΩ (black) and 1335 Ω (violet) for methanol@SURMOF.

Table SI1: The parameters of the reference circuit describing the experimental impedance data *Z*(*f*). The reference circuit is shown in Figures 3 and SI5. The fit equation is

$$(f) = \frac{1}{1\Big/\left(R + \left(\frac{1}{\sqrt{i * 2\pi * f * d}}\right)\right) + (i * C * 2\pi * f)^{x}}$$

. The variables are: frequency *f*, ohmic resistance *R*, capacity *C* with phase parameter *x* and Warburg parameter *d*.

	R (MΩ)	*C* (F)	*d*	*x*
ethanol in spiropyran-MOF	131.11	1.06E-16	1.43E-17	0.57
ethanol in merocyanine-MOF	2325.26	1.75E-14	9.09E-20	0.75
methanol in spiropyran-MOF	89.20	2.69E-16	1.86E-17	0.59
methanol in merocyanine-MOF	1317.90	1.45E-14	3.03E-19	0.74
water in spiropyran-MOF	3.45	4.96E-15	1.74E-14	0.50
water in merocyanine-MOF	279.52	7.28E-13	1.92E-17	0.82

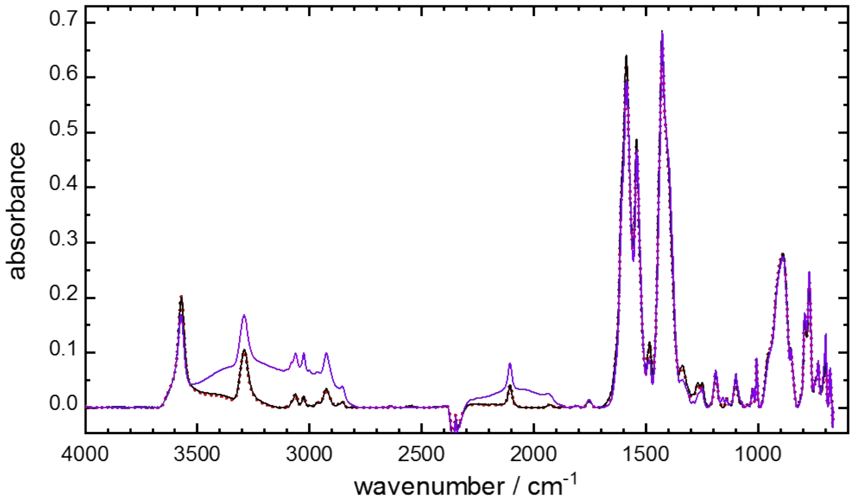


Figure SI6: Infrared spectra of the Cu_2(SP-BPDC)$_2$(dabco) SURMOF. The spectrum of the empty SURMOF is shown as red dotted line, the D_2O loaded SURMOF in the spiropyran form is shown as black solid line. The violet line is from the D_2O-loaded sample upon UV-irradiation, i.e. in the merocyanine form.

References

1. Agramunt, J.; Saltor, L.; Pedroso, E.; Grandas, A., Compatibility between the cysteine-cyclopentenedione reaction and the copper(I)-catalyzed azide-alkyne cycloaddition. *Organic & Biomolecular Chemistry* **2018,** *16* (47), 9185-9190.