Supporting Information -
Photoswitching in nanoporous, crystalline solids: An experimental and theoretical study for azobenzene linkers incorporated in metal-organic frameworks

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Supporting Information 1 – Structure and X-ray diffraction

Figure SI1: Structure of MOF Cu$_2$(AzoBPDC)$_2$(BiPy) (a, b) and MOF Cu$_2$(NDC)$_2$(AzoBiPy) (c, d) are shown with the azobenzene side groups in the trans state (a, c) and with the azobenzene in the cis state (b, d). The Cu atoms are plotted yellow, O red, C grey and N blue. H is not shown.
Figure SI2: X-ray diffraction (XRD). Out-of-plane and in-plane XRD data of Cu$_2$(AzoBPDC)$_2$(BiPy) (a) and Cu$_2$(NDC)$_2$(AzoBiPy) (b) compared with the simulated data. X-ray diffractometers of type Bruker D8 Advance and Bruker D8 Discover with an X-ray radiation of 0.154 nm wavelength were used for the out-of-plane and in-plane measurements.

Figure SI3: Out-of-plane X-ray diffraction (XRD) of Cu$_2$(AzoBPDC)$_2$(BiPy), Cu$_2$(NDC)$_2$(AzoBiPy) and Cu$_2$(BPDC)$_2$(AzoBiPyB) – pristine and after UV-irradiation. No significant changes of the positions or intensities of the XRD reflexes could be found.
Supporting Information 2 – Synthesis of AzoBiPyB and Photoswitching in Cu$_2$(bdc)$_2$(AzoBiPyB)

**General methods.** All reagents and solvents employed here were commercially available and used as supplied without further purification. Thin-layer chromatography (TLC) was carried out on silica gel plates (Silica gel 60, F254, Merck) with detection by UV. Purifications were performed with preparative chromatography using normal-phase silica gel (Silica gel 60, 230-400 mesh, Merck). Dipyridylazobenzene (DPAB or AzoBiPyB) and its precursors were characterized with nuclear magnetic resonance (NMR) spectroscopy, high resolution mass spectrometry (HRMS), infra-red spectroscopy (IR), UV-visible spectroscopy (UV-Vis) and elemental analysis. NMR spectra were recorded on a Bruker AM 500 spectrometer (500 MHz for $^1$H / 125 MHz for $^{13}$C), as solutions in CDCl$_3$. Chemical shifts, $\delta$, were quoted in parts per million (ppm) and were referenced to solvent residual peak as internal standard. The following abbreviations were used to describe peak patterns when appropriate: d = doublet, and m = multiplet. Coupling constants, $J$, are reported in Hertz unit (Hz). Mass spectra were recorded with a Finnigan MAT 95 (70 eV) spectrometer under electron impact (EI) conditions. The molecular fragments were quoted as the relation between mass and charge (m/z). The abbreviation [M$^+$] refers to the molecular ion. IR spectra were recorded with a FTIR Bruker IFS 88 spectrometer, using the attenuated total reflection technique (ATR). The absorption band positions are given in wave numbers $\nu$ in cm$^{-1}$. UV-Visible spectra were measured on a Cary 300 UV-Visible Spectrometer, Varian, Agilent Technologies.

**Synthesis of (E)-4,4'-((phenyldiazenyl)-1,4-phenylene)dipyrindine (dipyridylazobenzene, DPAB or AzoBiPyB)**

Scheme: 1,4-dibromo-2-nitrosobenzene (1). 3-chloroperoxybenzoic acid (m-CPBA) (70-75%) (4.76 g, 20.00 mmol, 2 eq) was dissolved in dry dichloromethane (60 mL), 2,5-dibromoaniline (2.51 g, 10.00 mmol, 1 eq) was added at 0°C under argon and the reaction mixture was stirred at 0°C for 1h. A solution of sodium carbonate (2.33 g, 22.00 mmol, 2.2 eq) in water (250 mL) was added and the reaction mixture was allowed to room temperature. Organic layer was separated, washed with water and brine, dried over magnesium sulfate, filtrated and evaporated under reduced pressure. The residue was purified with column chromatography (silica gel, 10% n-hexane in dichloromethane) to give (1) as a yellow solid (1.57 g, 59%). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ = 7.88 (d, 1H, $J$ = 8.5 Hz, $C^5$H), 7.65 (dd, 1H, $J$ = 8.5 Hz, $J$ = 2.5 Hz, $C^6$H), 6.33 (d, 1H, $J$ = 2.5 Hz, $C^3$H) ppm. $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ = 160.2 ($C^2$), 138.7 ($C^3$H), 136.8 ($C^4$H), 131.6 ($C^5$), 122.4 ($C^6$), 112.8 ($C^7$H) ppm. IR (ATR): $\nu$ = 3076, 1566, 1454, 1387, 1316 cm$^{-1}$. MS (EI): m/z = 265 [M$^+$], 235 [M$^+$-NO]. HRMS (EI): m/z C$_6$H$_3$Br$_2$NO, calcd.: 262.8581, found: 262.8584. Elemental analysis (%) (C$_6$H$_3$Br$_2$NO): calcd. C: 27.20, H: 1.14, N: 5.29; found C: 27.24, H: 1.11, N: 5.44.
(E)-1-(2,5-dibromophenyl)-2-phenyldiazene (2). Aniline (320 µL, 3.51 mmol, 1 eq) was added to a solution of 1,4-dibromo-2-nitrosobenzene (1) (1.03 g, 3.86 mmol, 1.1 eq) in acetic acid (25 mL) and the reaction mixture was stirred at 40°C for 24 h. The reaction mixture was cooled to room temperature, then concentrated under reduced pressure. Acetic acid (5 mL) was added to the residue and the suspension was filtrated; the solid obtained was washed with a few milliliters of acetic acid and dried to give (2) as a red-orange solid (0.87 g, 73%). 

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta = 8.00-7.98$ (m, 2H, $CHPh$), 7.83 (d, 1H, $J = 2.5$ Hz, $CHAr$), 7.62 (d, 1H, $J = 8.5$ Hz, $CHAr$), 7.55-7.53 (m, 3H, $CHPh$), 7.44 (dd, 1H, $J = 8.5$ Hz, $J = 2.5$ Hz, $CHAr$) ppm.

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 152.5$ ($CIV$-N=N), 150.3 ($CIV$-N=N), 135.0 ($CHAr$), 134.5 ($CHAr$), 132.3 ($CHPh$), 129.4 ($CHPh$), 124.6 ($CIV$-Br), 123.8 ($CHPh$), 122.2 ($CIV$-Br), 121.2 ($CHAr$) ppm.

IR (ATR): $\nu = 3080, 1484, 1443, 1368, 1307, 1287, 1068, 1032$ cm$^{-1}$. UV-Vis (CH$_2$Cl$_2$): $\lambda = 323$ nm. MS (EI): $m/z = 340$ [M$^+$]. HRMS (EI): $m/z$ C$_{12}$H$_8$Br$_2$N$_2$, calcd.: 337.9054, found: 337.9053. Elemental analysis (%) (C$_{12}$H$_8$Br$_2$N$_2$): calcd. C: 42.39, H: 2.37, N: 8.24; found C: 41.49, H: 2.19, N: 8.02.

(E)-4,4'-(2-(phenyldiazenyl)-1,4-phenylene)dipyridine (dipyridylazobenzene, DPAB or AzoBiPyB). (E)-1-(2,5-dibromophenyl)-2-phenyldiazene (2) (0.51 g, 1.50 mmol, 1 eq), 4-pyridylboronic acid (0.55 g, 4.50 mmol, 3 eq), tetrakis(triphenylphosphine)palladium(0) (87 mg, 0.08 mmol, 0.05 eq) and sodium carbonate (1.27 g, 12.00 mmol, 8 eq) were added in a degassed mixture of toluene-dioxane-H$_2$O (50 mL, 2/2/1) under argon. The mixture was heated at 85°C for 72 h under argon. The reaction mixture was cooled to room temperature, organic solvents were removed under reduced pressure. The resulting aqueous suspension was extracted with dichloromethane. The organic phase was washed with water, then dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified with column chromatography (silica gel, 25% dichloromethane in ethyl acetate) to give (DPAB) as a red solid (0.23 g, 46%). 

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta = 8.74$ (d, 2H, $J = 6.0$ Hz, $CHPy$), 8.71 (d, 2H, $J = 6.0$ Hz, $CHPy$), 8.09 (d, 1H, $J = 2.0$ Hz, $CHPy$), 7.87 (dd, 1H, $J = 8.0$ Hz, $J = 2.0$ Hz, $CHPy$), 7.83-7.81 (m, 2H, $CHPh$), 7.71 (d, 1H, $J = 8.0$ Hz, $CHPy$), 7.64 (d, 2H, $J = 6.0$ Hz, $CHPy$), 7.53-7.50 (m, 3H, $CHPh$), 7.46 (d, 2H, $J = 6.0$ Hz, $CHPy$) ppm. 

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 152.7$ ($CIV$-N=N), 150.6 ($CHPy$), 150.0 ($CIV$-N=N), 149.3 ($CHPh$), 147.3 ($CIV$), 146.4 ($CIV$), 139.6 ($CIV$), 139.0 ($CIV$), 131.9 ($CHAr$), 131.4 ($CHPh$), 129.5 ($CHAr$), 129.4 ($CHPh$), 125.7 ($CHPy$), 123.6 ($CHAr$), 121.8 ($CHPy$), 114.9 ($CHPh$) ppm. IR (ATR): $\nu = 3025, 1589, 1546, 1467, 1381, 1201, 1152$ cm$^{-1}$. UV-Vis (CH$_2$Cl$_2$): $\lambda = 276, 323$ nm. MS (EI): $m/z = 336$ [M$^+$], 231 [M$^+$-C$_6$H$_5$N$_2$]. HRMS (EI): $m/z$ C$_{22}$H$_{16}$N$_4$, calcd.: 336.1375, found: 336.1374. Elemental analysis (%) (C$_{22}$H$_{16}$N$_4$): calcd. C: 78.55, H: 4.79, N: 16.66; found C: 78.06, H: 4.69, N: 16.09.
Figure SI4: Structure and X-ray diffractogram of Cu$_2$(BDC)$_2$(AzoBiPyB) SURMOF. The structures of MOF of type Cu$_2$(BDC)$_2$(AzoBiPyB) is shown with the azobenzene side groups in the trans state (a) and with the azobenzene in the cis state (b). The Cu atoms are plotted yellow, O red, C grey and N blue. H is not shown. c) Out-of-plane and in-plane XRD data of Cu$_2$(BDC)$_2$(AzoBiPyB) grown on a gold surface modified with an MUD SAM compared with the simulated data. Although Cu$_2$(NDC)$_2$(AzoBiPy) would allow a more direct comparison with Cu$_2$(BPDC)$_2$(AzoBiPy), we use Cu$_2$(BPDC)$_2$(AzoBiPyB), due to the insufficient crystallinity of the Cu$_2$(NDC)$_2$(AzoBiPyB) SURMOFs, synthesized under not yet optimized conditions.
Figure SI5: UV-vis spectra of and QCM uptake by Cu₂(BDC)₂(AzoBiPyB) SURMOF. a) Compared are the UV-vis spectra of the pristine samples, i.e. before the samples were exposed to any light (black lines), after UV irradiation for 20 min (blue lines) and after irradiation with red light for 3 h (red lines). b) The uptake of butanediol by Cu₂(BDC)₂(AzoBiPyB) was measured without (black) and after (blue) UV irradiation. The uptake amount increases by about 20% when irradiated with UV light. The error bar at 1.5h represents the standard deviation.