

A Series of Photoswitchable Azobenzene-Containing Metal-Organic Frameworks with Variable Adsorption Effect

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S1: Synthesis of AzoTPDC.

Synthesis of **AzoTPDC** is displayed in Figure S11. Azobenzene derivative **2** was prepared via *Mills* reaction from a freshly prepared nitrosobenzene **1** and corresponding aniline. Methyl ester **3** was obtained by a *Suzuki* type coupling reaction of azobenzene derivative **2** with 4-(methoxycarbonyl)phenylboronic acid. It is subsequent hydrolysis provided the target **AzoTPDC** compound as an orange solid in 93% yield.

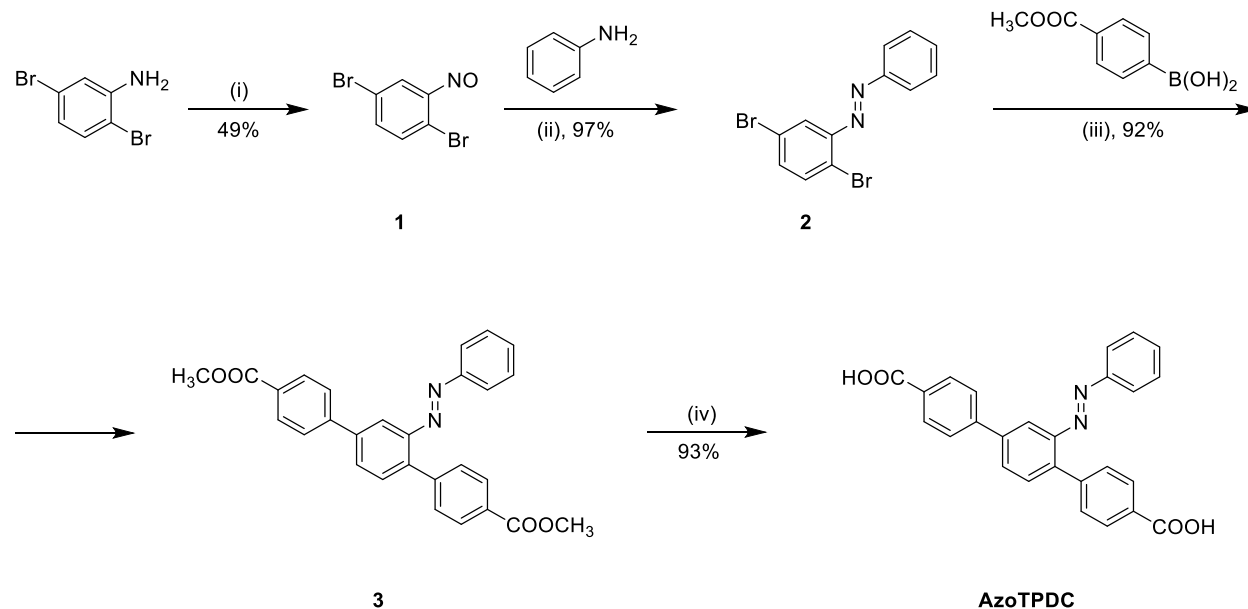


Figure S1: Synthesis of AzoTPDC. Reagents and conditions: (i) Oxone®, dichloromethane, water; (ii) acetic acid; (iii) PdCl₂(dppf), CsF, dioxane, water; (iv) a) KOH, THF, water, b) HCl.

Experimental part

Materials. All starting materials and reagents were obtained from commercial suppliers and used without further purification. TLC was performed on Silica gel 60 F₂₅₄ plates (Merck), spots were detected by fluorescence quenching under UV light at 254 nm, and/or staining with appropriate solutions (anisaldehyde, phosphomolybdic acid). Column chromatography was performed on Silica gel 60 (0.040-0.063 mm, Merck). All experimental manipulations with anhydrous solvents were carried out in flame-dried glassware under inert atmosphere of argon. Degassed solvents were obtained by three cycles of the freeze-pump-thaw. 1,4-Dibromo-2-nitrosobenzene **1** and (*E*)-1-(2,5-dibromophenyl)-2-phenyldiazenylbenzene **2** were prepared similarly to published procedures.¹

Equipment and Measurements. NMR spectra were recorded on a Bruker Avance 500 spectrometer at 25 °C in CDCl₃, or *d*₆-DMSO. ¹H NMR (500.16 MHz) spectra were referenced to the solvent residual proton signal (CDCl₃, δ_H = 7.26 ppm; DMSO-*d*₆, δ_H = 2.50 ppm). ¹³C NMR (125.78 MHz) spectra with total decoupling of protons were referenced to the solvent (CDCl₃, δ_C = 77.16 ppm, DMSO-*d*₆, δ_C = 39.51 ppm). For correct assignment of both ¹H and ¹³C NMR spectra, the ¹H-¹H COSY, ¹³C DEPT-135, HSQC and HMBS experiments were performed. Analytical samples were dried at 40 - 100 °C under reduced pressure (10⁻² mbar). Melting points were measured with a Büchi Melting point B-540 apparatus and are not corrected. Elemental analyses were obtained using a Vario Micro Cube CHNS analyzer.

Dimethyl (*E*)-2'-(phenyldiazenyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (3**)** In a 250 mL oven-dried Schlenk flask (*E*)-1-(2,5-dibromophenyl)-2-phenyldiazenylbenzene **2** (1.20 g, 3.53 mmol), and cesium fluoride (6.40 g, 42.13

mol) were dissolved in the mixture of dioxane (60 mL) and water (15 mL). The reaction mixture was purged with argon for 30 min before the addition of 4-(methoxycarbonyl)phenylboronic acid (1.91 g, 10.61 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (433 mg, 0.53 mmol). The reaction mixture was degassed and heated at 90 °C for 3 h under argon atmosphere. The reaction progress was checked by TLC (CH₂Cl₂:EtOAc = 3:1). After cooling, dioxane was distilled off. The residue was diluted with dichloromethane (200 mL), passed through a pad of silica gel (80 g), and washed with dichloromethane (400 mL). After extraction with water (100 mL) and drying with magnesium sulfate, the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (900 g) in the gradient of hexane : dichloromethane (1:1) - dichloromethane to afford the title molecule **3** (1.46 g) as an orange solid in 92% yield (R_f = 0.48, dichloromethane). Compound characterization data are corresponding to the literature.² ¹H NMR (500 MHz, CDCl₃) δ ppm: 3.94 (s, 3H, CH₃), 3.95 (s, 3H, CH₃), 7.43-7.49 (m, 3H, C^{3'''}, C^{4'''}, C^{5'''}H), 7.58 (dd, J = 8.4 Hz, J = 1.7 Hz, 2H, C^{2,6}H), 7.68 (d, J = 8.1 Hz, 1H, C^{6'}H), 7.77 (dd, J = 8.5 Hz, J = 1.8 Hz, 2H, C^{2'',6''}H), 7.79 (dd, J = 8.1 Hz, J = 1.7 Hz, 2H, C^{2''',6'''}H), 7.82 (dd, J = 8.1 Hz, J = 2.0 Hz, 1H, C^{5'}H), 8.03 (d, J = 1.9 Hz, 1H, C^{3'}H), 8.11 (dd, J = 8.4 Hz, J = 1.7 Hz, 2H, C^{3,5}H), 8.14 (dd, J = 8.4 Hz, J = 1.7 Hz, 2H, C^{3'',5''}H). ¹³C NMR (125.8 MHz, CDCl₃) δ ppm: 52.4 (CH₃), 114.9 (C^{3'}H), 123.6 (C^{2'',6''}H), 127.4 (C^{2''',6'''}H), 129.2 (C^{3,5}H, C^{4'}), 129.3 (C^{4''}), 129.4 (C^{3''',5'''}H), 129.6 (C^{5'}H), 130.4 (C^{3'',5''}H), 131.1 (C^{2,6}H), 131.55 (C^{6'}H), 131.62 (C^{4'''}H), 139.9 (C^{1'}), 140.7 (C^{4'}), 143.3 (C¹), 144.6 (C^{1''}), 150.1 (C^{2'}), 152.9 (C^{1'''}), 167.1 (CO^(\rightarrow 4'')), 167.3 (CO^(\rightarrow 4''')). Anal. Calcd. for C₂₈H₂₂N₂O₄ (450.49): C, 74.65; H, 4.92; N, 6.22. Found: C, 74.88; H, 4.85; N, 6.31.

(E)-2'-(Phenyldiazenyl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (AzoTPDC) This compound was synthesized using a modified procedure published in the literature.² A 500 mL flask equipped with a condenser was charged with methyl ester **3** (500 mg, 1.1 mmol) and tetrahydrofuran (220 mL). To an orange solution was added an aqueous solution (12 mL) of KOH (1.85 g, 33 mmol), and the reaction mixture was heated at 75 °C for 30 h. After cooling an orange precipitate was dissolved in water (50 mL), THF was distilled off under the vacuum and the resulting orange solution was acidified with diluted aq. HCl (2 M) to pH ~ 2. An orange solid was filtered off, washed with an excess of water (500 mL), dichloromethane (100 mL), diethyl ether (100 mL), air and vacuum dried to provide the target compound **AzoTPDC** (462 mg) as an orange solid in 93% yield. ¹H NMR (500 MHz, DMSO-*d*₆) δ ppm: 7.50-7.60 (m, 3H, C^{4'''}H, C^{3'',5''}H), 7.63 (dd, J = 7.7 Hz, 2H, C^{2,6}H), 7.77 (m, 2H, C^{2'',6''}H), 7.80 (m, 1H, C^{6'}H), 7.90 (dd, J = 7.7 Hz, 2H, C^{2''',6'''}H), 8.00-8.11 (m, 6H, C^{3'}H, C^{5'}H, C^{3,5}H, C^{3''',5'''}H), 12.99 (bs, 2H, COOH). ¹³C NMR (125.8 MHz, DMSO-*d*₆) δ ppm: 114.0 (C^{3'}H), 122.9 (C^{2''',6'''}H), 127.0 (C^{2'',6''}H), 128.8 (C^{3,5}H), 129.5 (C^{3'',5''}H), 129.7 (C^{5'}H), 129.8 (C^{4'}), 130.1 (C^{3'',5''}H), 130.2 (C^{4''}), 130.8 (C^{2,6}H), 131.7 (C^{6'}H), 131.8 (C^{4'''}H), 139.1 (C^{1'}), 139.6 (C^{4'}), 142.0 (C¹), 143.0 (C^{1''}), 149.2 (C^{2'}), 152.2 (C^{1'''}), 167.1 (CO^(\rightarrow 4'')), 167.2 (CO^(\rightarrow 4''')). Anal. Calcd. for C₂₆H₁₈N₂O₄ (422.44): C, 73.92; H, 4.30; N, 6.63. Found: C, 74.35; H, 4.49; N, 6.52.

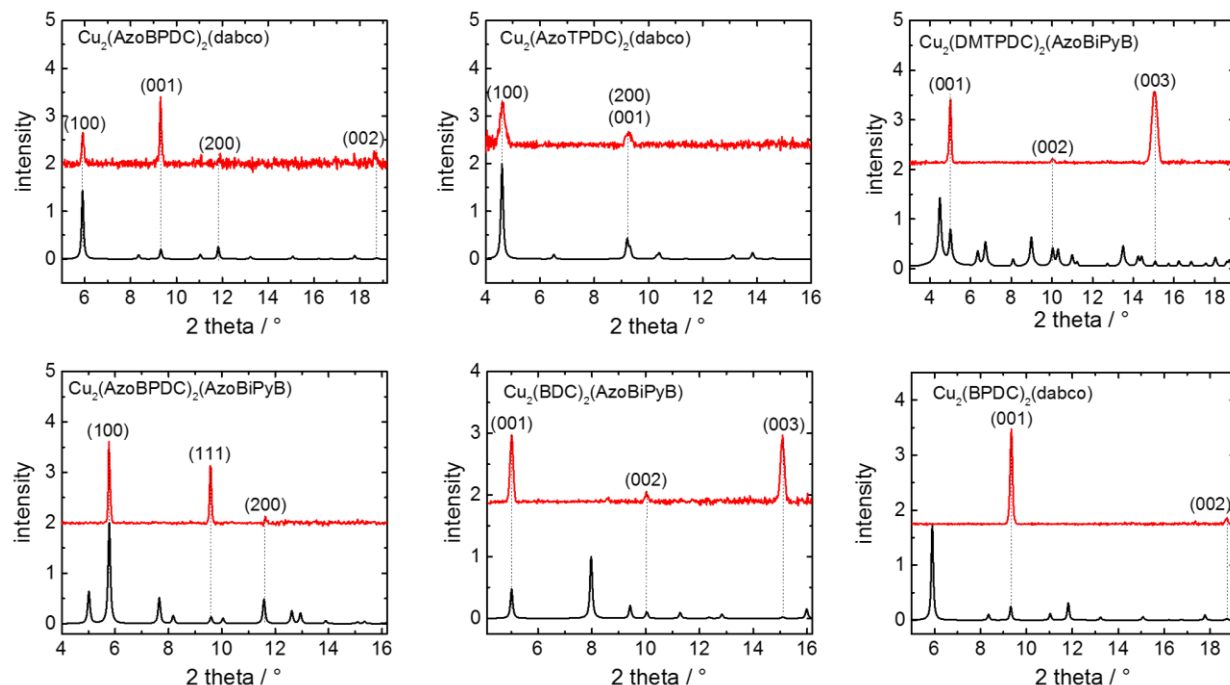


Figure S2: Out-of-plane X-ray diffractograms (XRDs) of the series of SURMOF samples. The names of the SURMOF structures are labelled in the plots. The red diffractograms were measured with a Bruker D8 Advance diffractometer using $\text{Cu}_{K\alpha}$ radiation (0.154 nm wavelength). The black data are the calculated powder diffractograms of the respective structures. While $\text{Cu}_2(\text{DMTPDC})_2(\text{AzoBiPyB})$, $\text{Cu}_2(\text{BDC})_2(\text{AzoBiPyB})$ and $\text{Cu}_2(\text{BPDC})_2(\text{dabco})$ were grown in (001) orientation on the substrate, $\text{Cu}_2(\text{AzoBPDC})_2(\text{dabco})$, $\text{Cu}_2(\text{AzoTPDC})_2(\text{dabco})$ and $\text{Cu}_2(\text{AzoBPDC})_2(\text{AzoBiPyB})$ SURMOFs were grown not exclusively oriented, i.e. these MOF thin films possess domains with different orientations. Since the pores of these MOF structures are large enough allowing the uptake of butanol along all directions, the crystalline orientation of the pillared-layer MOFs has no tremendous impact in the adsorption capacity. For more details on the XRD of oriented pillared-layer SURMOFs and the fact that not all reflexes are measured in the out-of-plane geometry, we refer to ref.³⁻⁶

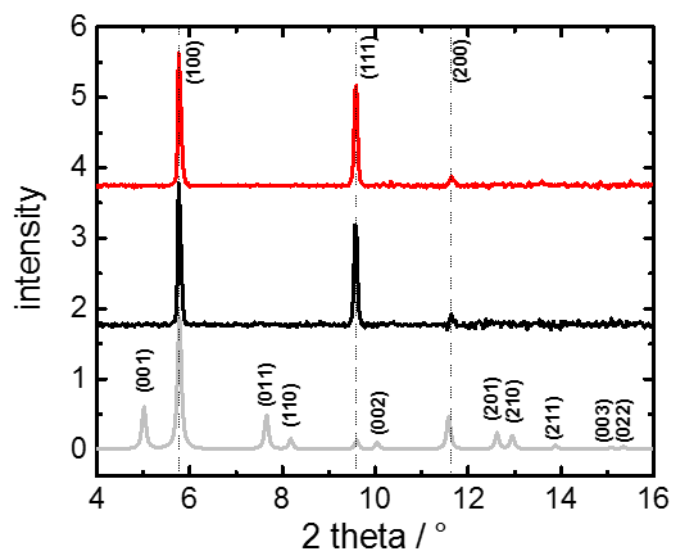


Figure S3: X-ray diffractogram of $\text{Cu}_2(\text{AzoBPDC})_2(\text{AzoBiPyB})$ SURMOF before (*trans*, black) and after (*cis*, red) UV irradiation for 20 min. The positions of the diffraction peaks are identical, i.e. are unaffected by the *trans-cis* isomerization. The relative peak intensities slightly change by less than 8 %, presumably due to small changes of the XRD form factor. The diffractograms were measured with a Bruker D8 Advance diffractometer using $\text{Cu}_{K\alpha}$ radiation (0.154 nm wavelength). The grey line is the calculated powder diffractogram with the labelled reflexes.

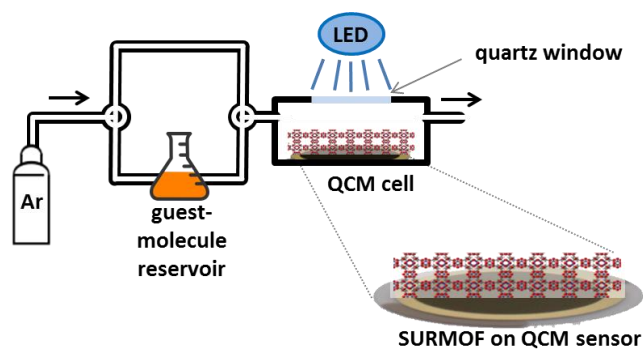


Figure S4: Setup for the QCM uptake experiments. A gas flow system where the carrier gas flows through the QCM cell, i.e. over the SURMOF on the QCM sensor, is used for the uptake experiments. The carrier gas flow (here: argon) can be enriched with the vapor of the guest molecules by passing through the (liquid) reservoir of the guest molecules. By means of an LED, the SURMOF on the QCM sensor can be directly irradiated with UV or vis light through the quartz glass window of the QCM cell.⁷

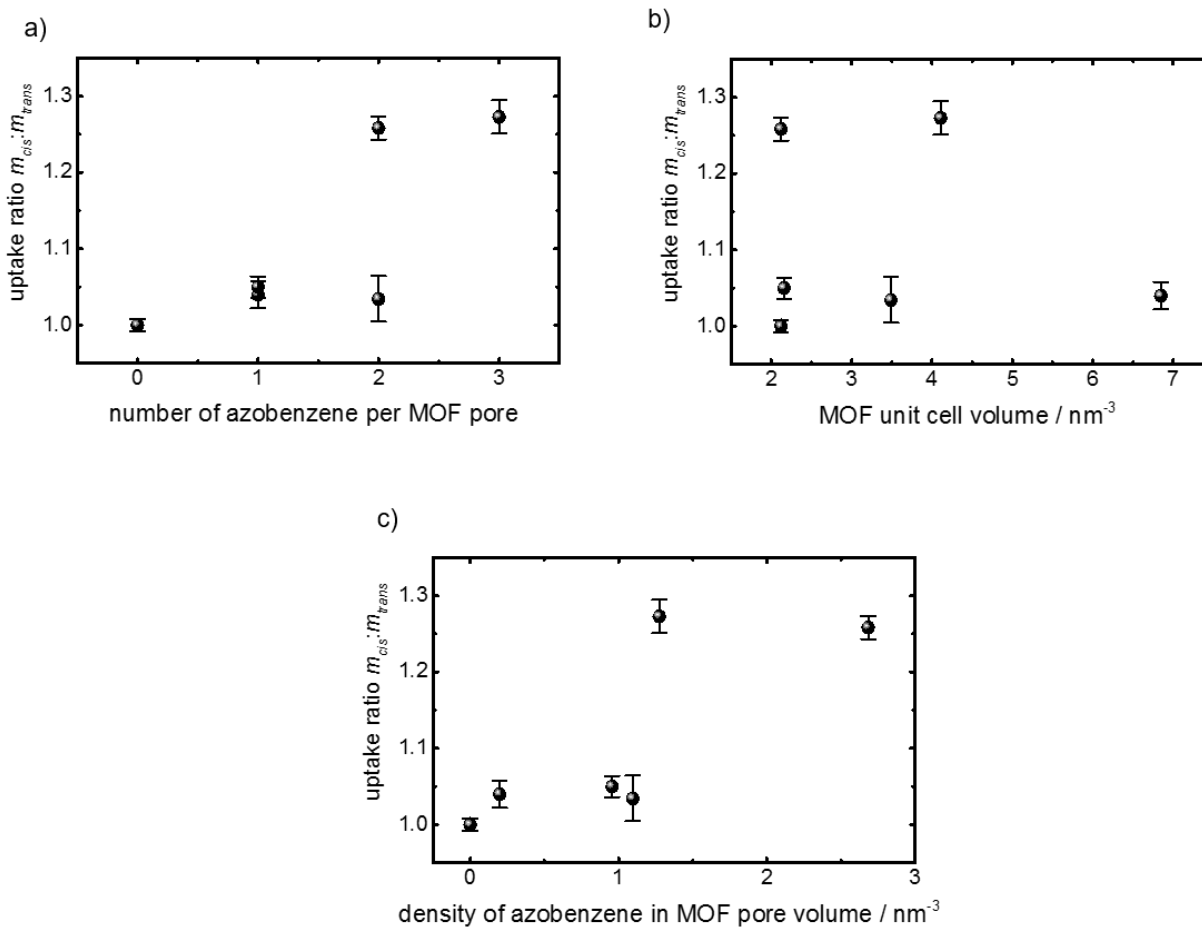


Figure S5: The switching effect, i.e. the ratio of the butanol uptake amounts by the azobenzene-SURMOFs in the *cis* and in the *trans* state, $m_{cis} : m_{trans}$, versus a) the number of the azobenzene moieties per unit cell, b) the volume of the unit cell and c) density of azobenzene per void MOF pore volume. The void MOF pore volume is calculated from the volume of the MOF unit cell minus the van-der-Waals-Volume of the atoms.

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