

## Supporting Information:

### ***Cis-to-Trans* Isomerization of Azobenzene Investigated by Using Thin Films of Metal-Organic Frameworks**

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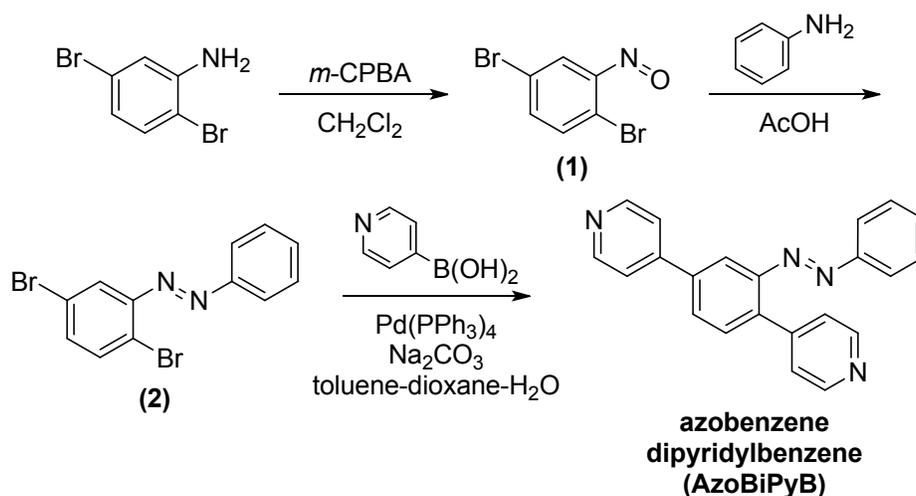
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#### **Supporting Information 1 – Synthesis of AzoBiPyB and DMTPDC**

**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). The linkers AzoBiPyB and DMTPDC, and their 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 <sup>1</sup>H / 125 MHz for <sup>13</sup>C), as solutions in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub>. 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: s = singlet, d = doublet, m = multiplet, and br = broad. 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<sup>+</sup>] 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<sup>-1</sup>. UV-Visible spectra were measured on a Cary 300 UV-Visible Spectrometer, Varian, Agilent Technologies.

### Synthesis of (*E*)-4,4'-(2-(phenyldiazenyl)-1,4-phenylene)dipyridine (AzoBiPyB).



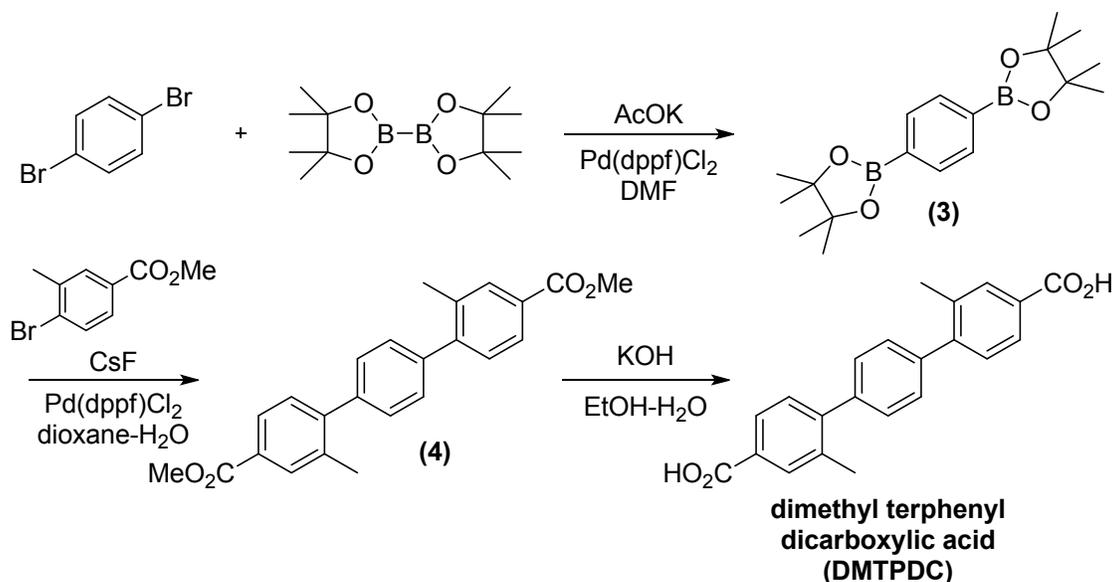
Scheme S1. Three-steps synthesis of AzoBiPyB linker

**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%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.88 (d, 1H, *J* = 8.5 Hz, C<sup>5</sup>H), 7.65 (dd, 1H, *J* = 8.5 Hz, *J* = 2.5 Hz, C<sup>6</sup>H), 6.33 (d, 1H, *J* = 2.5 Hz, C<sup>3</sup>H) ppm. <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ = 160.2 (C<sup>2</sup>), 138.7 (C<sup>5</sup>H), 136.8 (C<sup>6</sup>H), 131.6 (C<sup>4</sup>), 122.4 (C<sup>1</sup>), 112.8 (C<sup>3</sup>H) ppm. IR (ATR): ν = 3076, 1566, 1454, 1383, 1260, 1190 cm<sup>-1</sup>. MS (EI): *m/z* = 265 [M<sup>+</sup>], 235 [M<sup>+</sup>-NO]. HRMS (EI): *m/z* C<sub>6</sub>H<sub>3</sub>Br<sub>2</sub>NO, calcd.: 262.8581, found: 262.8584. Elemental analysis (%) (C<sub>6</sub>H<sub>3</sub>Br<sub>2</sub>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-phenyldiazenene (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 24h. 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%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.00-7.98 (m, 2H, CH<sub>Ph</sub>), 7.83 (d, 1H, *J* = 2.5 Hz, CH<sub>Ar</sub>), 7.62 (d, 1H, *J* = 8.5 Hz, CH<sub>Ar</sub>), 7.55-7.53 (m, 3H, CH<sub>Ph</sub>), 7.44 (dd, 1H, *J* = 8.5 Hz, *J* = 2.5 Hz, CH<sub>Ar</sub>) ppm. <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ = 152.5 (C<sup>IV</sup>-N=N), 150.3 (C<sup>IV</sup>-N=N), 135.0 (CH<sub>Ar</sub>), 134.5 (CH<sub>Ar</sub>), 132.3 (CH<sub>Ph</sub>), 129.4 (CH<sub>Ph</sub>), 124.6 (C<sup>IV</sup>-Br), 123.8 (CH<sub>Ph</sub>), 122.2 (C<sup>IV</sup>-Br), 121.2 (CH<sub>Ar</sub>) ppm. IR (ATR): ν = 3080, 1484, 1443, 1368, 1307, 1287, 1068, 1032 cm<sup>-1</sup>. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ = 323 nm. MS (EI): *m/z* = 340 [M<sup>+</sup>]. HRMS (EI): *m/z* C<sub>12</sub>H<sub>8</sub>Br<sub>2</sub>N<sub>2</sub>, calcd.: 337.9054, found: 337.9053. Elemental analysis (%) (C<sub>12</sub>H<sub>8</sub>Br<sub>2</sub>N<sub>2</sub>): 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 (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<sub>2</sub>O (50 mL, 2/2/1) under argon. The mixture was heated at 85°C for 72h 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 **(AzoBiPyB)** as a red solid (0.23 g, 46%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.74 (d, 2H, *J* = 6.0 Hz, CH<sub>Py</sub>), 8.71 (d, 2H, *J* = 6.0 Hz, CH<sub>Py</sub>), 8.09 (d, 1H, *J* = 2.0 Hz, CH<sub>Ph</sub>), 7.87 (dd, 1H, *J* = 8.0 Hz, *J* = 2.0 Hz, CH<sub>Ph</sub>), 7.83-7.81 (m, 2H, CH<sub>Ph</sub>), 7.71 (d, 1H, *J* = 8.0 Hz, CH<sub>Ph</sub>), 7.64 (d, 2H, *J* = 6.0 Hz, CH<sub>Py</sub>), 7.53-7.50 (m, 3H, CH<sub>Ph</sub>), 7.46 (d, 2H, *J* = 6.0 Hz, CH<sub>Py</sub>) ppm. <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ = 152.7 (C<sup>IV</sup>-N=N), 150.6 (CH<sub>Py</sub>), 150.0 (C<sup>IV</sup>-N=N), 149.3 (CH<sub>Py</sub>), 147.3 (C<sup>IV</sup>), 146.4 (C<sup>IV</sup>), 139.6 (C<sup>IV</sup>), 139.0 (C<sup>IV</sup>), 131.9 (CH<sub>Ar</sub>), 131.4 (CH<sub>Ph</sub>), 129.5 (CH<sub>Ar</sub>), 129.4 (CH<sub>Ph</sub>), 125.7 (CH<sub>Py</sub>), 123.6 (CH<sub>Ar</sub>), 121.8 (CH<sub>Py</sub>), 114.9 (CH<sub>Ph</sub>) ppm. IR (ATR): ν = 3025, 1589, 1546, 1467, 1381, 1201, 1152 cm<sup>-1</sup>. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ = 276, 323 nm. MS (EI): *m/z* = 336 [M<sup>+</sup>], 231 [M<sup>+</sup>-C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>]. HRMS (EI): *m/z* C<sub>22</sub>H<sub>16</sub>N<sub>4</sub>, calcd.: 336.1375, found: 336.1374. Elemental analysis (%) (C<sub>22</sub>H<sub>16</sub>N<sub>4</sub>): calcd. C: 78.55, H: 4.79, N: 16.66; found C: 78.06, H: 4.69, N: 16.09.

### Synthesis of 2,2''-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (DMTPDC).



Scheme S2. Three-steps synthesis of DMTPDC linker

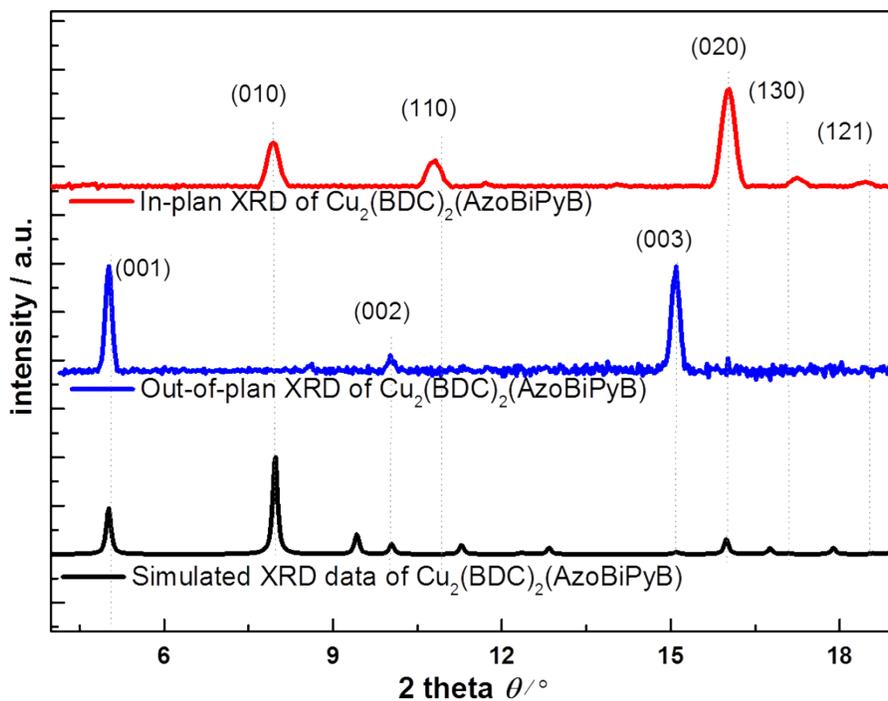
**1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (3).** 1,4-dibromobenzene (2.36 g, 10.00 mmol, 1 eq), bis(pinacolato)diboron (7.62 g, 30.00 mmol, 3 eq), Pd(dppf)Cl<sub>2</sub> (0.49 g, 0.60 mmol, 0.06 eq), and potassium acetate (5.89 g, 60.00 mmol, 6 eq) were dissolved in degassed dimethylformamide (70

mL) under argon atmosphere. The mixture was heated at 85°C for 48h. The reaction mixture was cooled to room temperature, then added to water (100 mL) before being extracted with dichloromethane (3 x 75 mL). Combined organic layers were washed with water and brine, then dried over sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, 0% to 10% ethyl acetate in *n*-hexane) to give (**3**) as a pale-green solid (2.89 g, 88%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.80 (s, 4H, CH<sub>Ar</sub>), 1.35 (s, 24H, CH<sub>3</sub>(Bpin)) ppm. <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ = 134.0 (CH<sub>Ar</sub>), 84.0 (C<sup>IV</sup>), 83.6 (C<sup>IV</sup>), 25.2 (CH<sub>3</sub>(Bpin)) ppm. IR (ATR): ν = 2977, 1522, 1466, 1392, 1328, 1277, 1172 cm<sup>-1</sup>. MS (EI): *m/z* = 330 [M<sup>+</sup>], 315 [M<sup>+</sup>-CH<sub>3</sub>]. HRMS (EI): *m/z* C<sub>18</sub>H<sub>28</sub>B<sub>2</sub>O<sub>4</sub>, calcd.: 330.2174, found: 330.2174.

**Dimethyl 2,2''-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (4).** 1,4-bis(pinacolatoboron)benzene (**3**) (1.50 g, 4.55 mmol, 1 eq), methyl 4-bromo-3-methylbenzoate (2.29 g, 10.00 mmol, 2.2 eq), Pd(dppf)Cl<sub>2</sub> (0.37 mg, 0.46 mmol, 0.10 eq) and cesium fluoride (4.14 g, 27.27 mmol, 6 eq) were dissolved in a degassed dioxane-water mixture (180 mL; 2/1) under argon atmosphere. The mixture was refluxed for 24h. The reaction mixture was cooled to room temperature, then added to water (250 mL) before being extracted with dichloromethane (3 x 100 mL). Combined organic layers were washed with water and brine, then dried over magnesium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, 40% to 70% dichloromethane in *n*-hexane) to give (**4**) as a white solid (1.51 g, 89%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.99 (d, 2H, *J* = 1.5 Hz, CH<sub>Ar</sub>), 7.93 (dd, 2H, *J* = 8.0 Hz, *J* = 1.5 Hz, CH<sub>Ar</sub>), 7.39 (s, 4H, CH<sub>Ph</sub>), 7.36 (d, 2H, *J* = 8.0 Hz, CH<sub>Ar</sub>), 3.95 (s, 6H, CO<sub>2</sub>CH<sub>3</sub>), 2.38 (s, 6H, ArCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ = 167.3 (CO<sub>2</sub>CH<sub>3</sub>), 146.2 (C<sup>IV</sup>), 140.1 (C<sup>IV</sup>), 135.8 (C<sup>IV</sup>), 131.7 (CH<sub>Ar</sub>), 130.1 (CH<sub>Ar</sub>), 129.2 (C<sup>IV</sup>), 128.9 (CH<sub>Ph</sub>), 127.2 (CH<sub>Ar</sub>), 52.3 (CO<sub>2</sub>CH<sub>3</sub>), 20.7 (ArCH<sub>3</sub>) ppm. IR (ATR): ν = 3053, 2948, 1717, 1606, 1484, 1432, 1394, 1281, 1132, 1041 cm<sup>-1</sup>. MS (EI): *m/z* = 374 [M<sup>+</sup>], 343 [M<sup>+</sup>-OCH<sub>3</sub>]. HRMS (EI): *m/z* C<sub>24</sub>H<sub>22</sub>O<sub>4</sub>, calcd.: 374.1518, found: 374.1511. Elemental analysis (%) (C<sub>24</sub>H<sub>22</sub>O<sub>4</sub>): calcd. C: 76.99, H: 5.92; found C: 76.39, H: 5.97.

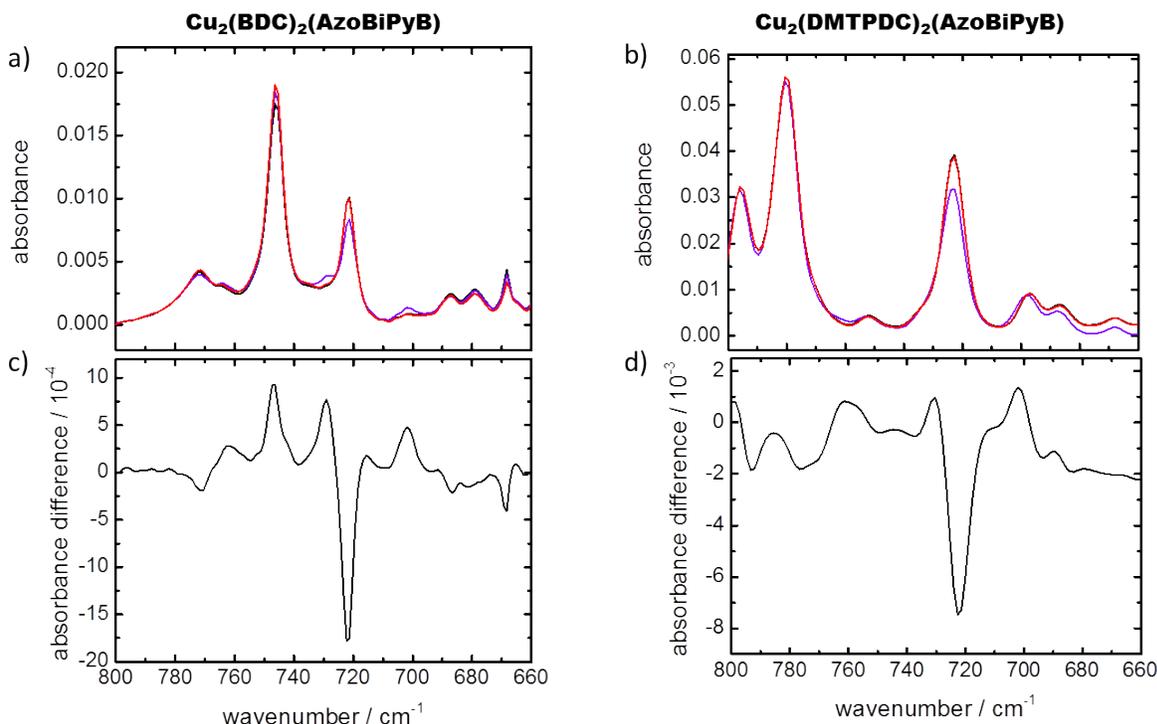
**2,2''-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid (DMTPDC).** A solution of dimethyl 2,2''-dimethyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**4**) (0.20 g, 0.53 mmol, 1 eq) in a degassed 1 M KOH solution in ethanol-water (1/1, 10 mL) was refluxed under argon for 3h. The solution was cooled in ice, and concentrated HCl (10 mL) was added. A pale pink precipitate was formed, filtered, washed extensively with water, and dried under vacuum to give (DMTPDC) as a slight pink solid (0.12 g, 63%). <sup>1</sup>H-NMR (500 MHz, DMSO): δ = 12.95 (br-s, 2H, CO<sub>2</sub>H), 7.91 (s, 2H, CH<sub>Ar</sub>), 7.84 (d, 2H, *J* = 7.0 Hz, CH<sub>Ar</sub>), 7.48 (s, 4H, CH<sub>Ph</sub>), 7.40 (d, 2H, *J* = 7.0 Hz, CH<sub>Ar</sub>), 2.35 (s, 6H, ArCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (125 MHz, DMSO): δ = 167.2 (CO<sub>2</sub>H), 145.1 (C<sup>IV</sup>), 139.4 (C<sup>IV</sup>), 135.3 (C<sup>IV</sup>), 131.3 (CH<sub>Ar</sub>), 129.9 (CH<sub>Ar</sub>), 129.7 (C<sup>IV</sup>), 128.8 (CH<sub>Ph</sub>), 127.0 (CH<sub>Ar</sub>), 20.2 (ArCH<sub>3</sub>) ppm. IR (ATR): ν = 3035, 2985, 1679, 1607, 1566, 1425, 1310, 1260, 1132 cm<sup>-1</sup>. MS (EI): *m/z* = 346 [M<sup>+</sup>]. HRMS (EI): *m/z* C<sub>22</sub>H<sub>18</sub>O<sub>4</sub>, calcd.: 346.1205, found: 346.1199. Elemental analysis (%) (C<sub>22</sub>H<sub>18</sub>O<sub>4</sub>): calcd. C: 76.29, H: 5.24; found C: 74.55, H: 5.33.

## Supporting Information 2: In-plane and out-of-plane XRD of $\text{Cu}_2(\text{BDC})_2(\text{AzoBiPyB})$



**Figure SI2: X-ray diffractogram of  $\text{Cu}_2(\text{BDC})_2(\text{AzoBiPyB})$  SURMOF.** Out-of-plane and in-plane XRD data of  $\text{Cu}_2(\text{BDC})_2(\text{AzoBiPyB})$  grown on a gold surface modified with an MUD SAM compared with the simulated data. (See ref.1)

### Supporting Information 3: Difference of *cis* and *trans* spectra



**Figure SI3: IRRA spectra of  $\text{Cu}_2(\text{BDC})_2(\text{AzoBiPyB})$  (a) and  $\text{Cu}_2(\text{DMTPDC})_2(\text{AzoBiPyB})$  (b) SURMOFs and the difference of the respective *cis* and *trans* spectra (c and d).** a) and b) The IR spectra of the pristine SURMOFs (black), i.e. with the azobenzene groups in the *trans* state, of the SURMOF irradiated with UV light for about 20 min (violet), i.e. some azobenzene groups photoisomerized to the *cis* state, and after waiting overnight (red), i.e. all azobenzene groups relaxed to the *trans* state, are shown. The spectra of the pristine sample and upon waiting overnight are virtually identical. (see figure 2 in the main text of the article.) The difference of the *cis* and *trans* spectra are shown in c) and d). Upon UV irradiation, the decreases of the *trans* bands at  $\sim 720 \text{ cm}^{-1}$  as well as the increase of the *cis* bands at about  $705 \text{ cm}^{-1}$  are visible.

### References:

- (1) Wang, Z.; Heinke, L.; Jelic, J.; Cakici, M.; Dommaschk, M.; Maurer, R. J.; Oberhofer, H.; Grosjean, S.; Herges, R.; Bräse, S.; Reuter, K.; Wöll, C. *Phys. Chem. Chem. Phys.* **2015**, *17*, 14582