# **Supporting Information**

# **Crystalline Nanochannels with Pendant Azobenzene Groups: Steric or Polar Effects on Gas Adsorption and Diffusion?**

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### 1. Materials and Methods

#### Materials

Unless otherwise noted, all of the commercially available chemicals were purchased from Wako Pure Chemical Industries Ltd, Tokyo Chemical Industry Co. Ltd. (TCI), and Sigma-Aldrich, and used without further purification.

#### Methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL model JNM-ECA 500 spectrometer operating at 500.00 MHz and 125.65 MHz for <sup>1</sup>H and <sup>13</sup>C NMR, respectively, using partially or non-deuterated solvent residues as internal references. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker model Autoflex<sup>TM</sup> speed spectrometer in the reflector mode using dithranol as a matrix. Electronic absorption spectra were recorded on a JASCO type V-670 spectrophotometer. Powder X-ray diffraction (PXRD) measurements were carried out on a Rigaku model RINT-ULTIMA III X-ray powder diffractometer equipped with a Cu sealed tube ( $\lambda = 1.54056$  Å), which was operated at 40 kV and 40 mA. The PXRD data were collected in a range of 3° to 50° in  $2\theta$  by a step-scan mode with a step size of 0.05°. Thermogravimetric analysis (TGA) was conducted on a Mettler-Toledo model TGA/SDTA851° in a temperature range from 25 °C to 1000 °C at a heating rate of 5 °C  $min^{-1}$  under N<sub>2</sub> with a flow rate of 20 mL  $min^{-1}$ . Single crystal X-ray diffraction (SCXRD) measurements were recorded on a Rigaku model VariMax Dual. Optical images were taken on a KEYENCE model VHX-S550E. UV or visible light irradiation was performed on an Asahi Spectra LAX-C100 with a 100 W heatless xenon light source. The gas sorption isotherm measurements for  $CO_2$  (99.995%) and Ar (> 99.9999%) were conducted by using an automatic volumetric adsorption apparatus (BELSORP-max12-G-SP; MicrotracBEL Corp.) equipped with a cryostat system. A weighed sample (~30 mg) of powdery <sup>Azo</sup>MOF was placed in a metallic copper cell and then kept under high vacuum for 2 h to remove guest molecules. The sample cell was then placed on a cryostat system and evacuated at  $< 10^{-2}$  Pa. The CO<sub>2</sub> and Ar adsorption measurements were conducted at 195 K and 87 K, respectively. The internal pressure change was monitored, and the amounts of  $CO_2$  and Ar adsorbed were evaluated at each equilibrium point.

#### 2. Synthesis



# 2.1. Synthesis of <sup>Azo</sup>LH<sub>2</sub> (Compound 3)

### 2.1.1 Synthesis of Compound 1

A mixture of DMF (22 mL) and H<sub>2</sub>O (22 mL) was degassed by Ar bubbling for 30 min before the addition of a solid mixture of 2,5-dibromoaniline (4.1 g, 16.3 mmol), (4-(methoxylcarbonyl)phenyl)boronic acid (17.6 g, 98.3 mmol), Na<sub>2</sub>CO<sub>3</sub> (6.9 g, 65.2 mmol), and Pd(OAc)<sub>2</sub> (26.3 mg, 0.08 mmol). The resulting mixture was subjected to freeze-pump-thaw cycles and then stirred at 60 °C for 26 h under Ar. After the reaction mixture was allowed to cool to room temperature, water (50 ml) was poured into the mixture, which was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL x 3). The organic extract was evaporated to dryness under reduced pressure, and the residue was subjected to recrystallization from EtOH, affording **1** as a light yellow solid substance (yield: 4.4 g; 86% based on 2,5-dibromoaniline). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 22 °C, ppm):  $\delta$  8.12 (4H, m, Ar-H), 7.67 (2H, d, *J* = 8 Hz, Ar-H), 7.03 (1H, d, *J* = 2 Hz, 8 Hz, Ar-H), 7.03 (1H, d, *J* = 2 Hz, Ar-H), 3.96 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 3.94 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 3.89 (2H, br, NH<sub>2</sub>).

## 2.1.2 Synthesis of Compound 2

To a suspension of **1** (2.0 g, 5.54 mmol) in AcOH (100 mL), after freeze-pump-thaw cycles, was added nitrosobenzene (2.34 g, 22.2 mmol), and the mixture was stirred at 80 °C for 22 h under Ar. The reaction mixture was allowed to cool to room temperature,

and then evaporated to dryness under reduced pressure. The residue was suspended in water (50 mL), and an insoluble fraction was separated by filtration and dried under reduced pressure. A light yellow solid substance thus obtained was washed with hot EtOH and subjected to recrystallization from THF, affording a pale yellow solid substance (yield: 1.96 g, 79% based on 1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 22 °C, ppm):  $\delta$  8.15 (4H, m, Ar-H), 8.05 (1H, s, J = 2 Hz, Ar-H), 7.84 (1H, dd, J = 2 Hz, 8 Hz), 7.82 (1H, d, J = 3 Hz, Ar-H), 7.80 (2H, d, J = 3 Hz, Ar-H), 7.78 (1H, d, J = 2 Hz), 7.70 (1H, d, J = 8 Hz, Ar-H), 7.60 (2H, d, J = 8 Hz, Ar-H), 7.48 (3H, m, Ar-H), 3.97 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 3.96 (3H, s, CO<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 22 °C, ppm):  $\delta$  167.12, 166.90, 152.67, 149.84, 144.42, 143.08, 140.54, 139.72, 131.41, 131.34, 130.85, 130.24, 129.44, 129.21, 129.03, 128.98, 127.16, 123.38,114.71, 52.23.

#### 2.1.3 Synthesis of Compound 3

To a THF (10 mL)/MeOH (10 mL) solution of **2** (0.25 g, 0.56 mmol) was added an aqueous solution (10 mL) of KOH (1.15 g, 205 mmol), and the mixture was refluxed for 24 h. The reaction mixture was allowed to cool to room temperature and evaporated to dryness under reduced pressure. The residue was dissolved in water (80 mL) at 70 °C, and the resulting reddish orange solution was acidified with diluted aq. HCl (1 M) until no further precipitate formed (pH ~ 3). A yellow-colored solid substance was collected by filtration, washed with a large volume of water, and dried under reduced pressure (yield: 0.23 g, 99% based on **2**). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 22 °C, ppm):  $\delta$  8.06 (6H, m, Ar-H), 7.94 (2H, d, *J* = 8 Hz, Ar-H), 7.84 (1H, d, *J* = 8 Hz, Ar-H), 7.80 (1H, d, *J* = 2 Hz, Ar-H), 7.79 (1H, d, *J* = 2 Hz, Ar-H), 7.66 (2H, d, *J* = 8 Hz, Ar-H), 7.58 (3H, m, Ar-H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 22 °C, ppm):  $\delta$  167.29, 167.16, 152.27, 149.37, 143.08, 142.14, 139.76, 139.18, 131.88, 131.82, 130.94, 130.32, 130.23, 129.89, 129.85, 129.66, 128.92, 127.14, 123.04, 114.10.

# 2.2 Synthesis of AzoMOFs

To a glass vial (5 mL) containing a DMF (2 mL) solution of a mixture of anhydrous ZrCl<sub>4</sub> (12 mg, 0.05 mmol) and benzoic acid (0, 10, 20, 30, 40 or 50 equiv. with respect to ZrCl<sub>4</sub>) was added <sup>Azo</sup>LH<sub>2</sub> (22 mg, 0.05 mmol), and the mixture was sonicated for 5 min. In order to obtain large (> 100  $\mu$ m) crystals of the target <sup>Azo</sup>MOF, deionized water (0, 4.5, 6,

10, 20, 30 or 40 equiv. with respect to ZrCl<sub>4</sub>) was added to the reaction mixture. The resulting mixture was transferred to a tightly capped glass tube ( $\phi = 6$  mm) being kept at 120 °C for 24 h. After the reaction mixture was allowed to cool to room temperature, reddish orange crystals adopting an octahedral shape were obtained. A single crystal appropriate for the structural analysis was subjected to SCXRD. The as-synthesized crystals were collected and washed with DMF. Then, the crystals were immersed successively in DMF at 40 °C for 24 h and in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C for 2 days, and the resultant suspension was subjected to centrifugation. The solid substance thus isolated was dried at 60 °C under reduced pressure, affording reddish orange powdery crystals of <sup>Azo</sup>MOF (yield: 15 mg, 55% based on <sup>Azo</sup>LH<sub>2</sub>), which thermally decomposed at around 450 °C according to a thermogravimetric analysis.

### 3. X-Ray Crystallography

A single crystal of <sup>Azo</sup>MOF was mounted using a MiTeGen MicroMount and subjected to single crystal X-ray diffractometry, where the diffraction data were collected at 100 K on a Rigaku model VariMax Dual diffractometer equipped with a fine-focus sealed-tube X-ray source ( $\lambda = 0.71075$  Å) and a confocal graphite monochromator. The structure was solved by direct methods and refined by full-matrix least-squares cycles in SHELX97. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C were located at geometrically calculated positions and refined with isotropic thermal parameters. Because solvent molecules included in the MOF channels were heavily disordered, the *SQUEEZE* command in *PLATON* was used in the structure refinement. The crystallographic data for <sup>Azo</sup>MOF were summarized in Figure S8 and Table S1.

# 4. Quantification of Photoisomerization in AzoMOF

# 4.1 Determination of the *cis*-isomer contents in <sup>Azo</sup>MOFs

A <sup>Azo</sup>MOF sample (1.0 mg) was poured into a D<sub>2</sub>O solution of DCl (0.025 mL, 35 wt% in D<sub>2</sub>O) for digestion and then diluted with DMSO- $d_6$  (0.65 mL). The resulting solution containing <sup>Azo</sup>LH<sub>2</sub> was subjected shortly to <sup>1</sup>H NMR spectroscopy to determine the *cis*-isomer content of <sup>Azo</sup>LH<sub>2</sub>. As shown in Figure S6, no accelerated *cis*-to-*trans* backward isomerization of <sup>Azo</sup>LH<sub>2</sub> was observed so long as the measurement was done in

10 min. In Figure S11, the signals at  $\delta$  7.6– $\delta$  7.8 ppm are assigned to the *trans*-isomer, while those at  $\delta$  6.5– $\delta$  7.4 ppm are assigned to the *cis*-isomer. These well separated sets of signals were integrated to obtain the *cis*-isomer content (*cis*%) defined as  $I_{cis}/(I_{trans} + I_{cis})$ .

## 4.2 Repetitive photoisomerization cycles.

A pulverized <sup>Azo</sup>MOF<sup>1%</sup> (~15 mg) sample was sandwiched by two glass plates such that the powdery sample was as thin and homogeneous as possible. The resulting sandwiched sample was turned upside down occasionally upon exposure to UV ( $365 \pm 10$ nm) and visible (420–480 nm) light for 45 and 20 min, respectively. As shown in Figure S12, the photoisomerization occurred reversibly and reproducibly.

# 5. Supporting Figures



**Figure S1.** <sup>1</sup>H NMR spectrum of 1 at 25 °C in CDCl<sub>3</sub>. Signals at  $\delta$  7.26 (asterisk) and 1.56 ppm (triangle), are due to CHCl<sub>3</sub> and water, respectively.



**Figure S2.** <sup>1</sup>H NMR spectrum of **2** at 25 °C in CDCl<sub>3</sub>. Signals at  $\delta$  7.26 (asterisk) and 1.56 ppm (triangle) are due to CHCl<sub>3</sub> and water, respectively.



**Figure S3.** <sup>1</sup>H NMR spectrum of **3** at 25 °C in DMSO- $d_6$ . Signals at  $\delta$  2.56 (asterisk) and 3.33 (triangle) ppm are due to partially deuterated DMSO and water, respectively.



**Figure S4.** Electronic absorption spectra of  $^{Azo}LH_2$  in DMSO (20  $\mu$ M) at 25 °C upon irradiation with (a) UV light (365 ± 10 nm) and (b) visible light (420–480 nm). The insets in (a) and (b) represent absorption spectra magnified in a range from 400 nm to 580 nm. Arrows indicate the directions of the spectral changes.



**Figure S5.** (a) <sup>1</sup>H NMR spectra of <sup>Azo</sup>*L*H<sub>2</sub> (1.5 mM) at 25 °C in DMSO-*d*<sub>6</sub>. The initial black-colored spectrum (*cis*% = 1%) changed to a blue-colored one (*cis*% = 75%) upon irradiation with UV light ( $365 \pm 10 \text{ nm}$ ), and then to an orange-colored one (*cis*% = 18%) upon subsequent irradiation with visible light (420–480 nm). Changes in the *cis*-isomer content of <sup>Azo</sup>*L*H<sub>2</sub> with time at 25 °C upon irradiation with UV ( $365 \pm 10 \text{ nm}$ ) (b) and visible light (420–480 nm) (c), respectively.

=> The photostationary state upon irradiation with UV light (365 ± 10 nm) was established in 90 min with the *cis*-isomer content of 75%, while that upon irradiation with visible light (420–480 nm) was established within 10 min with the *cis*-isomer content of 18%.



**Figure S6.** Changes in the *cis*-isomer contents of  $^{Azo}LH_2$  (1.5 mM) with time in DMSO-*d*<sub>6</sub> (0.65 mL) with (filled circles) and without (open circles) aq. DCl (35 wt%, 25  $\mu$ L) at 22 °C in the dark. For the method to evaluate the *cis*-isomer contents, see pages S5–S6, section 4.1.

=> No accelerated backward (*cis*-to-*trans*) isomerization of <sup>Azo</sup>LH<sub>2</sub> occurs in the quick digestion process (< 10 min) established in the present work (see pages S5–S6, section 4.1).</p>



**Figure S7.** Effects of (a) benzoic acid and (b) water on the formation of  $^{Azo}MOF$  from  $^{Azo}LH_2$  and ZrCl<sub>4</sub> in DMF at 120 °C. PXRD patterns of  $^{Azo}MOFs$  formed with (a) varying equiv. of benzoic acid (0–50 equiv.) and 4.5 equiv. of water, and (b) 30 equiv. of benzoic acid and varying equiv. of water (0–40 equiv.) with respect to ZrCl<sub>4</sub>.

=> The best synthetic result was obtained with 30 equiv. of benzoic acid and 4.5 equiv. of water.



**Figure S8.** Structural details of <sup>Azo</sup>MOF revealed by a single-crystal X-ray diffraction analysis: (a) a  $Zr_6O_4(OH)_4(CO_2)_{12}$  cluster, (b) the positional disorder of a phenylene moiety in <sup>Azo</sup> $L^{2-}$ , (c) a triangular window, (d) a tetrahedral pore, and (e) an octahedral pore in <sup>Azo</sup>MOF.



**Figure S9.** Pore size distribution of  $^{Azo}MOF^{1\%}$  (black) together with that of  $^{Azo}MOF^{15\%}$  (blue) obtained by irradiation of  $^{Azo}MOF^{1\%}$  with UV light.

=> No substantial change in pore size distribution indicates that <sup>Azo</sup>MOF possesses a highly robust metal-organic framework.



**Figure S10.** Diffuse reflectance spectra of <sup>Azo</sup>MOF at 25 °C in the solid state upon irradiation with (a) UV ( $365 \pm 10 \text{ nm}$ ) and (b) visible (420–480 nm) light. Arrows denote the directions of the spectral changes.



**Figure S11.** <sup>1</sup>H NMR spectra at 25 °C of digested solutions of <sup>Azo</sup>MOF<sup>1%</sup> before (black) and after 30-min exposure to UV light (<sup>Azo</sup>MOF<sup>21%</sup>, blue), followed by 20-min exposure to visible light (<sup>Azo</sup>MOF<sup>6%</sup>, orange). The method of digestion was described in section 4.1 on pages S5–S6.

=> As shown in Figure S12, the photoisomerization occurred reversibly and reproducibly.



**Figure S12.** Repetitive photoisomerization cycles of <sup>Azo</sup>MOF in the solid state upon alternate irradiation with UV light ( $365 \pm 10 \text{ nm}$ ) for 45 min and visible light (420-480 nm) for 20 min. The same isomerization cycle was repeated twice more.

=> The photoisomerization occurred reversibly and reproducibly.



**Figure S13.** PXRD patterns of  $^{Azo}MOF^{1\%}$  before (black) and after UV-light exposure for 1, 2, and 12 h (blue), followed by visible-light exposure for 1, 2, and 4 h (orange) at 25 °C.

=> No substantial change in PXRD indicates that <sup>Azo</sup>MOF can maintain its crystallinity in the photochemical isomerization cycles.



**Figure S14.** Electronic absorption spectra of EB (5  $\mu$ M) in EtOH before (black) and after (blue) mixing with <sup>Azo</sup>MOF<sup>20%</sup> (0.5 mg) at 25 °C for 12 h in the dark followed by the removal of an insoluble fraction by filtration.

 $\Rightarrow$  The intensity loss corresponds to the amount of EB adsorbed onto  $^{Azo}MOF^{20\%}$ .



**Figure S15.** (a) Diffuse reflectance spectra of EB in the solid state before (black) and after (blue) the irradiation with UV light ( $365 \pm 10 \text{ nm}$ ) at 25 °C for 2 h. (b) Diffuse reflectance spectra of EB in the solid state before (black) and after (orange) the irradiation with visible light (420–480 nm) at 25 °C for 2 h.

=> These results indicate that EB is stable under irradiation with visible light but undergoes photodecomposition upon irradiation with UV light.



**Figure S16.** Diffuse reflectance spectra of EB mixed in the solid state with <sup>Azo</sup>MOFs having *cis*-isomer contents of 1% (black), 6% (orange), and 20% (blue). Here, EB is supposed to be adsorbed mostly on the outer surface of <sup>Azo</sup>MOFs.

=> No appreciable shift in a range from 500 to 600 nm (cf. see Figure 4b), indicating that what is observed in Figure 4b is indeed attributable to the spectral change of EB incorporated inside the pores of <sup>Azo</sup>MOF.



**Figure S17.** Fitting curves of the kinetic parameters of Ar at the inflection point ( $P/P_0 = 0.01$ ) (a) and of CO<sub>2</sub> at the inflection point ( $P/P_0 = 0.15$ ) (b) with a double-exponetial model.



**Figure S18.** Isosteric heats ( $Q_{st}$ ) of the adsorption of CO<sub>2</sub> in <sup>Azo</sup>MOF<sup>1%</sup> (black) and <sup>Azo</sup>MOF<sup>15%</sup> (blue) as a function of the uptake of CO<sub>2</sub>.

=> The  $Q_{st}$  value of the adsorption of CO<sub>2</sub> in <sup>Azo</sup>MOF<sup>15%</sup> was 38 kJ mol<sup>-1</sup> at zero coverage, which is larger than that in <sup>Azo</sup>MOF<sup>1%</sup> (29 kJ mol<sup>-1</sup>), indicating a higher affinity of CO<sub>2</sub> toward <sup>Azo</sup>MOF<sup>15%</sup> than <sup>Azo</sup>MOF<sup>1%</sup>.

# 6. Supporting Tables

	<sup>Azo</sup> MOF
Empirical Formula	$C_{120}H_{48}O_{32}Zr_6$
Formula Weight	2549.00
Crystal System	cubic
Space Group	Fm-3m
<i>a</i> (Å)	32.735 (12)
$V(\text{\AA}^3)$	35078 (22)
Ζ	4
R <sub>int</sub>	0.1843
$\mu$ (cm <sup>-1</sup> )	1.968
$D_{calcd}/g$	0.483
F(000)	5056
Goodness of Fit	0.953
Temperature (K)	100 (2)
Reflections Collected	9000
Independent Reflections	2012
$R$ (I > 2.00 $\sigma$ (I), all data)	0.0994
$R_{\rm w}$ (I > 2.00 $\sigma$ (I), all data)	0.2827

**Table S1.** Crystallographic data and structural refinement summary for <sup>Azo</sup>MOF

AzoMOF <sup>1%</sup>						Standard dev	riation ( $\sigma$ )
$P/P_0$	$w k_d^{1\%}$	${}^{P}k_{d}{}^{1\%}$	<b>R</b> <sup>2</sup>	$A_1$	A <sub>2</sub>	$\sigma(wk_d^{1\%})$	$\sigma(pk_d^{1\%})$
0.0030	0.0325	0.594	0.98	0.55	0.45	0.00259	0.07290
0.0059	0.0402	0.795	0.99	0.43	0.57	0.00269	0.05547
0.0087	0.0404	0.408	0.99	0.51	0.49	0.00344	0.04068
0.0116	0.0426	0.818	0.98	0.30	0.70	0.00420	0.04714
0.0200	0.0469	0.588	0.97	0.32	0.68	0.00724	0.05124
0.0410	0.0327	0.537	0.93	0.17	0.83	0.00810	0.04976
0.0570	0.0317	0.580	0.94	0.18	0.82	0.00897	0.04604
0.0725	0.0309	0.518	0.98	0.16	0.84	0.00190	0.02522
0.0884	0.0330	0.539	0.99	0.17	0.83	0.00204	0.02872
0.1100	0.0351	0.594	0.99	0.17	0.83	0.00164	0.02917
0.1352	0.0304	0.556	0.99	0.20	0.80	0.00155	0.03080
0.1520	0.0242	0.487	0.99	0.22	0.78	0.00650	0.06779
0.1667	0.0247	0.557	0.99	0.26	0.74	0.00105	0.02621
0.1820	0.0256	0.926	0.99	0.31	0.69	0.00109	0.05049
0.3100	0.0422	0.831	0.99	0.12	0.88	0.00158	0.05264
0.4210	0.0411	0.807	0.99	0.10	0.90	0.00162	0.04237
0.4740	0.0421	0.867	0.99	0.10	0.90	0.00140	0.04431
0.5260	0.0345	0.866	0.98	0.07	0.93	0.00185	0.04909
0.6300	0.0395	0.858	0.99	0.10	0.90	0.00126	0.04220
0.7360	0.0336	0.804	0.99	0.10	0.90	0.00160	0.03886
0.8450	0.0267	0.731	0.99	0.13	0.87	0.00102	0.03564
0.9500	0.0211	0.742	0.99	0.12	0.88	0.00070	0.03587

**Table S2.** Kinetic parameters of the adsorption isotherms of  $CO_2$  with  $^{Azo}MOF^{1\%}$ .

AzoMOF <sup>15%</sup>						Standard dev	viation ( $\sigma$ )
$P/P_0$	${}^{w}k_{d}{}^{15\%}$	${}^{P}k_{d}{}^{15\%}$	R <sup>2</sup>	$\mathbf{A}_1$	<b>A</b> <sub>2</sub>	$\sigma({}^{w}k_{d}{}^{15\%})$	$\sigma(pk_d^{15\%})$
0.0030	0.0026	0.364	0.99	0.39	0.61	0.00026	0.02530
0.0059	0.0025	0.386	0.99	0.37	0.63	0.00027	0.02735
0.0087	0.0026	0.450	0.98	0.36	0.64	0.00023	0.02557
0.0116	0.0025	0.485	0.93	0.26	0.74	0.00024	0.02758
0.0200	0.0028	0.559	0.99	0.28	0.72	0.00036	0.03383
0.0410	0.0029	0.655	0.92	0.25	0.75	0.00042	0.04044
0.0570	0.0028	0.703	0.95	0.23	0.77	0.00043	0.04351
0.0725	0.0028	0.669	0.93	0.21	0.79	0.00055	0.04705
0.0884	0.0030	0.727	0.90	0.23	0.77	0.00055	0.05475
0.1100	0.0028	0.802	0.99	0.19	0.81	0.00056	0.05480
0.1352	0.0026	0.456	0.99	0.23	0.77	0.00013	0.02555
0.1520	0.0030	0.744	0.94	0.27	0.73	0.00044	0.05649
0.1667	0.0029	0.721	0.93	0.32	0.68	0.00030	0.04729
0.1820	0.0039	0.610	0.95	0.31	0.69	0.00042	0.03726
0.3100	0.0034	0.854	0.98	0.20	0.80	0.00016	0.05264
0.4210	0.0032	0.422	0.99	0.11	0.89	0.00084	0.02271
0.4740	0.0036	0.462	0.99	0.10	0.90	0.00097	0.02756
0.5260	0.0044	0.529	0.99	0.06	0.94	0.00012	0.03319
0.6300	0.0047	0.481	0.99	0.06	0.94	0.00013	0.02288
0.7360	0.0048	0.519	0.99	0.04	0.96	0.00014	0.02410
0.8450	0.0047	0.566	0.99	0.03	0.97	0.00013	0.02584
0.9500	0.0042	0.558	0.99	0.04	0.96	0.00013	0.03676

**Table S3.** Kinetic parameters of the adsorption isotherms of  $CO_2$  with <sup>Azo</sup>MOF<sup>15%</sup>.

AzoMOF <sup>1%</sup>						Standard dev	viation ( $\sigma$ )
$P/P_0$	${}^{w}k_{d}{}^{1\%}$	${}^{p}k_{d}{}^{1\%}$	<b>R</b> <sup>2</sup>	$\mathbf{A}_{1}$	A <sub>2</sub>	$\sigma(wk_d^{1\%})$	$\sigma({}^{p}k_{d}{}^{1\%})$
0.0000	0.025	0.485	0.996	0.68	0.32	0.00091	0.04258
0.0003	0.030	0.524	0.997	0.69	0.31	0.00089	0.04147
0.0008	0.032	0.543	0.994	0.67	0.33	0.00131	0.05439
0.0011	0.033	0.628	0.996	0.63	0.37	0.00105	0.04205
0.0021	0.036	0.510	0.993	0.63	0.37	0.00177	0.05103
0.0031	0.037	0.527	0.995	0.63	0.37	0.00148	0.04232
0.0044	0.038	0.400	0.995	0.64	0.36	0.00198	0.04041
0.0060	0.043	0.703	0.993	0.52	0.48	0.00224	0.05437
0.0085	0.043	0.653	0.993	0.52	0.48	0.00218	0.04500
0.0123	0.034	0.348	0.989	0.44	0.56	0.00331	0.02910
0.0141	0.029	0.307	0.989	0.41	0.59	0.00291	0.02284
0.0179	0.029	0.343	0.992	0.40	0.60	0.00233	0.02049
0.0220	0.037	0.290	0.991	0.37	0.63	0.00199	0.01606
0.0282	0.020	0.364	0.990	0.34	0.66	0.00191	0.01970
0.0369	0.018	0.385	0.980	0.33	0.67	0.00230	0.02739
0.0474	0.027	0.460	0.980	0.37	0.63	0.00304	0.03486
0.0882	0.025	0.697	0.997	0.18	0.82	0.00063	0.03085
0.1126	0.027	0.775	0.998	0.13	0.87	0.00056	0.02719
0.1396	0.027	0.902	0.994	0.08	0.92	0.00091	0.04618
0.1714	0.025	0.873	0.990	0.07	0.93	0.00104	0.04036
0.2671	0.032	0.964	0.995	0.07	0.93	0.00096	0.04730
0.3191	0.027	1.047	0.990	0.03	0.97	0.00111	0.04760
0.4246	0.035	1.333	0.992	0.03	0.97	0.00132	0.08060
0.5812	0.028	1.191	0.990	0.03	0.97	0.00111	0.07818
0.7973	0.024	1.097	0.990	0.02	0.98	0.00120	0.04493

**Table S4.** Kinetic parameters of the adsorption isotherms of Ar with  $^{Azo}MOF^{1\%}$ .

AzoMOF <sup>15%</sup>					Standard dev	riation ( $\sigma$ )	
$P/P_0$	${}^{w}k_{d}{}^{15\%}$	${}^{p}k_{d}{}^{15\%}$	<b>R</b> <sup>2</sup>	$\mathbf{A}_{1}$	$\mathbf{A}_{2}$	$\sigma(wk_d^{15\%})$	$\sigma(pk_d^{15\%})$
0.0000	0.024	0.443	0.995	0.66	0.34	0.00097	0.03940
0.0003	0.029	0.470	0.993	0.66	0.34	0.00138	0.05024
0.0008	0.032	0.661	0.995	0.61	0.39	0.00119	0.04902
0.0011	0.032	0.481	0.993	0.65	0.34	0.00163	0.05159
0.0021	0.036	0.478	0.993	0.65	0.35	0.00192	0.05369
0.0031	0.039	0.480	0.993	0.66	0.34	0.00208	0.05722
0.0044	0.042	0.507	0.994	0.65	0.35	0.00206	0.05286
0.0060	0.045	0.568	0.989	0.56	0.44	0.00393	0.07611
0.0085	0.045	0.435	0.992	0.59	0.41	0.00307	0.04964
0.0123	0.044	0.347	0.992	0.51	0.49	0.00373	0.03302
0.0141	0.041	0.381	0.991	0.48	0.52	0.00345	0.03243
0.0179	0.037	0.353	0.990	0.43	0.57	0.00348	0.02796
0.0220	0.038	0.475	0.993	0.40	0.6	0.00255	0.02514
0.0282	0.031	0.392	0.989	0.37	0.63	0.00291	0.02460
0.0369	0.030	0.546	0.990	0.33	0.67	0.00261	0.02786
0.0474	0.027	0.460	0.980	0.37	0.63	0.00304	0.03486
0.0882	0.037	0.683	0.996	0.18	0.82	0.00105	0.02994
0.1126	0.041	0.781	0.992	0.12	0.88	0.00168	0.04543
0.1396	0.043	0.937	0.995	0.10	0.9	0.00133	0.06368
0.1714	0.046	0.895	0.993	0.09	0.91	0.00179	0.05970
0.2671	0.044	1.129	0.985	0.05	0.95	0.00225	0.12593
0.3191	0.044	1.022	0.980	0.04	0.96	0.00263	0.07172
0.4246	0.053	1.242	0.990	0.02	0.98	0.00295	0.10937
0.5812	0.046	1.126	0.990	0.02	0.98	0.00237	0.06279
0.7973	0.044	1.161	0.980	0.02	0.98	0.00268	0.06278

**Table S5.** Kinetic parameters of the adsorption isotherms of Ar with  $^{Azo}MOF^{15\%}$ .