<Supplementary Information>

Pore space partition of a fragile Ag(I)-carboxylate framework via post-synthetic linker insertion

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I. Experimental section

1. Materials and general procedures

All reagents and solvents were purchased from commercial sources and used without further purification. Elemental analyses (EA; C, H, and N) were conducted using an elemental analyzer, Flash 2000, at the Central Research Facilities of the Ulsan National Institute of Science and Technology, Korea. Fourier Transform-infrared (FT-IR) spectra were recorded as KBr pellets using a NICOLET iS 10 FT-IR spectrophotometer (4000–400 cm⁻¹). Powder X-ray diffraction (PXRD) data were recorded using a Bruker D2 Phaser automated diffractometer at room temperature with a step size of $2\theta = 0.02^{\circ}$. Nuclear magnetic resonance (NMR) spectra were obtained using a 400 MHz FT-NMR spectrometer. The UV-vis absorption of the dye molecules was monitored by measuring the spectra at specific time intervals. All UV-vis spectra were collected using a Cary 5000 (Agilent) UV-vis-NIR (200–3300 nm) spectrophotometer. All gas sorption isotherms were measured using a BELSROP-max (BEL Japan, Inc.) sorption system employing a standard volumetric technique to saturation pressure. The N₂ (purity 99.9999%) sorption isotherms were monitored at 77 K. The adsorption data in the pressure range of <0.1 P/P₀ were fit to the Brunauer-Emmett-Teller (BET) equation to determine the BET surface area. The CO₂ (purity 99.9999%) sorption isotherms were measured at 195, 273, and 298 K.

2. Preparation of AgBTB, AgBTB-dpey, AgBTB-dpt and AgBTB-bpy

AgBTB. A solid mixture of AgNO₃ (0.0878 g, 0.523 mmol) and 1,3,5-benzenetribenzoic acid (H₃BTB) (0.0498 g, 0.114 mmol) was dissolved in 5 mL *N*,*N*-diethylformamide (DEF) in a 20 mL glass vial and subsequently sonicated for 3 min. The tightly sealed vial was heated to 100 °C for 20 h, and slowly cooled to ambient temperature. The collected crystals were washed using *N*,*N*-dimethylformamide (DMF) and air-dried under ambient conditions for 12 h. Yield = 0.0697 g (62.6%). EA for $[Ag_3(BTB)] \cdot (DMF)_{1.5}(H_2O)_6$ (C_{31.5}H_{37.5}N_{1.5}O_{13.5}Ag₃, fw = 976.74 g/mol). Found (Calc.): C = 38.95 (38.78)%; H = 3.56 (3.87)%; N = 2.20 (2.15)%. IR spectrum of **1** (KBr, cm⁻¹): 3416 (vs, b), 3062 (w, b), 2923 (w, b), 2849 (w, b), 2802 (w), 2509 (w), 1936 (w), 1808 (w), 1664 (s), 1585 (s), 1544 (s), 1523 (s), 1543 (s), 1437 (m), 1379 (vs), 1305 (m, sh), 1252 (m), 1180 (m), 1135 (w), 1095 (m), 1061 (w),

1013 (m), 961 (w), 893 (w), 849 (m), 806 (m), 783 (s, sh), 772 (s), 701 (m), 662 (m), 608 (vw), 593 (vw), 574 (vw), 555 (vw), 539 (vw), 524 (vw), 496 (m), 469 (m), 438 (vw), 418 (vw).

AgBTB-dpey. First, 60–70 mg of single crystals of **AgBTB** were soaked in DMF and transferred into a 40 mL 10 mM 1,2-di(pyridin-4-yl)ethyne (dpey) DMF solution in a vial and kept under ambient condition for 4 d. The obtained ivory crystals were washed using fresh DMF more than three times and air-dried at ambient temperature for 1 h. The amount of dpey linker in **AgBTB-dpey** was estimated using the relative proton ratio of the dpey linker and BTB ligand in the ¹H NMR spectrum of **AgBTBdpey** crystals digested in DMSO-*d*₆ with a drop of aqueous D₂SO₄ solution and via EA. EA for [Ag₆(BTB)₂(dpey)_{0.84}]·(DMF)₃(H₂O)₁₁ (C_{73.08}H_{81.40}N_{4.68}O₂₆Ag₆, fw = 2088.53 g/mol). Found (Calc.): C = 41.58 (42.03)%; H = 3.47 (3.93)%; N = 3.59 (3.14)%.

AgBTB-dpt. **AgBTB-dpt** was obtained using the same procedure as for the preparation of **AgBTB-dpe but** with 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine (dpt) as a linker. The amount of dpt linker in **AgBTB-dpt** was estimated using the relative proton ratio of the dpt linker and BTB ligand in the ¹H NMR spectrum of the sample digested in DMSO- d_6 with 0.2 mL aqueous DCl solution and via EA. EA for [Ag₆(BTB)₂(dpt)_{0.74}]·(DMF)₁(H₂O)₈ (C_{65.88}H_{58.92}N_{5.44}O₂₁Ag₆, fw = 1910.05 g/mol). Found (Calc.): C = 41.50 (41.43)%; H = 3.26 (3.11)%; N = 3.94 (3.99)%.

AgBTB-bpy. **AgBTB-bpy** was obtained using the same procedure as for the preparation of **AgBTB-dpey** but with 4,4'-bipyridine (bpy) as a linker. The amount of bpy was estimated using the relative proton ratio of bpy linker and BTB ligand in the ¹H NMR spectrum of the sample digested in DMSO*d*₆ with a drop of aqueous DCl solution and via EA. EA for $[Ag_3(BTB)(bpy)_{0.8}] \cdot (DMF)_{1.5}(H_2O)_7$ (C₄₁H_{45.4}N_{3.6}O₁₃Ag₃, fw = 1119.71 g/mol). Found (Calc.): C = 42.18 (42.37)%; H = 3.31 (4.13)%; N = 4.33 (3.88)%.

3. Preparation of Ag(I)-MOFs for the gas sorption study

The pore space partitioned **AgBTB** crystals for the gas sorption study were prepared using methylene chloride (MC) solution instead of DMF. The **AgBTB** crystals were soaked in 10 mL of 1 or 2 mM MC solutions containing each dipyridyl linker for 2 days. The MC solution was replaced up to 4 times every other day with fresh the dipyridyl linker solution. The resulting **AgBTB-dpey(x)**, **AgBTB-dpt(x)**, and

AgBTB-bpy(**x**) samples were activated for gas sorption measurements at room temperature for 1 day. The '**x**' represents the volume of MC used for the linker insertion. Before activation, all samples were quickly washed with 80 mL of fresh MC (20 mL \times 4). The amount of dipyridyl linker was estimated using the relative proton ratio of dipyridyl linker and BTB ligand in the ¹H NMR spectrum of the sample digested in DMSO-*d*₆ with aqueous DCl (or D₂SO₄) solution and via EA after the gas sorption experiments

II. Crystallographic data collection and structure refinement

The diffraction data of **AgBTB**, **AgBTB-dpey**, and **AgBTB-bpy** single crystals coated with paratone-*N* oil were measured at 298 K using synchrotron radiation ($\lambda = 0.700$ or 0.800 Å) on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. The PAL BL2D-SMDC Program^{S1} was used for data collection and HKL3000sm (Ver. 703r)^{S2} was used for cell refinement, reduction, and absorption correction. The single crystal diffraction data of **AgBTB-dpt** coated with paratone-*N* oil were measured at 173 K with Mo K α radiation using an X-ray diffraction camera system equipped with an imaging plate and graphite crystal incident beam monochromator. RapidAuto software^{S3} was used for data collection and processing. All crystal structures were solved by a direct method and refined via full-matrix least-squares calculation using the SHELX software package.^{S4}

[Ag₃(BTB)(H₂O)_{0.70}] (AgBTB). Three silver atoms, one BTB ligand, and a ligated water molecule with 0.70 site occupancy were observed as an asymmetric unit. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U (C) with their coordinates allowed to ride on their respective atoms. The final refinement was performed via modification of the structure factors for the electron densities of the disordered solvents (3480 Å³, 45.1% of the total unit cell volume; 615 electrons correspond to ~15 DMF molecules per unit cell) using the SQUEEZE option in PLATON.^{S5} Refinement of the structure converged at a final *R*1 = 0.0768 and wR2 = 0.2134 for 3396 reflections with $I > 2\sigma(I)$; R1 = 0.1264 and wR2 = 0.2533 for all 7571 reflections. The largest difference peak and hole were 0.908 and -0.876 e·Å⁻³, respectively.

 $[Ag_6(BTB)_2(dpey)_{0.75}]$ (AgBTB-dpey). Six silver atoms, two BTB ligands, and one dpey linker at a Wyckoff position 2*b* of site symmetry 2 with 0.96 site occupancy, with the other dpey linker at a Wyckoff position 2*a* of site symmetry 2 with 0.55 site occupancy, and two DMF sites for a total of 1.37 site occupancies are observed as an asymmetric unit. Two different binding modes of dpey linkers reduce space group symmetry from *I*2/*a* of Ag-BTB to *I*2 of Ag-BTB-dpey. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U (C) with their coordinates allowed to ride on their respective atoms. The least-squares

refinement of the structural model was performed using displacement parameter restraints such as DELU, DFIX, FLAT, ISOR, and SIMU. The final refinement was performed via modification of the structure factors for the electron densities of the disordered solvents (1298 Å³, 17.7% of the total unit cell volume; 235 electrons correspond to ~6 DMF molecules per unit cell) using the SQUEEZE option in PLATON.^{S5} Refinement of the structure converged at a final R1 = 0.0519 and wR2 = 0.1420 for 7322 reflections with $I > 2\sigma(I)$; R1 = 0.0739 and wR2 = 0.1557 for all 10393 reflections. The largest difference peak and hole were 1.042 and -0.683 e·Å⁻³, respectively.

[Ag₆(BTB)₂(dpt)_{0.74}] (AgBTB-dpt). Six silver atoms, two BTB ligands, one dpt linker with a 0.74 site occupancy, and three DMF sites for a total of 1.69 site occupancies were observed as an asymmetric unit. All non-hydrogen atoms were refined anisotropically where the hydrogen atoms attached to the ligands were assigned isotropic displacement coefficients U(H) = 1.2U (C) and their coordinates allowed to ride on their respective atoms. The least-squares refinement of the structural model was performed using displacement parameter restraints such as DFIX, DANG, FLAT, ISOR, DELU, and SIMU. The final refinement was performed via modification of the structure factors for the electron densities of the disordered solvents (1213 Å³, 15.6% of the total unit cell volume; 642 electrons correspond to ~16 DMF molecules per unit cell) using the SQUEEZE option in PLATON.^{S5} Refinement of the structure converged at a final *R*1 = 0.1703, *wR*2 = 0.3946 for 7478 reflections with *I* > 2 σ (*I*); *R*1 = 0.2670, *wR*2 = 0.4501 for all 17170 reflections. The largest difference peak and hole were 7.595 and -1.552 e·Å⁻³, respectively.

 $[Ag_3(BTB)(bpy)_{0.80}]$ (AgBTB-bpy). Three silver atoms, one BTB ligand, one bpy linker with a 0.80 site occupancy, and one DMF molecule were observed as an asymmetric unit. All non-hydrogen atoms were refined anisotropically where the hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U (C) and their coordinates allowed to ride on their respective atoms. The least-squares refinement of the structural model was performed using displacement parameter restraints including DFIX, DANG, FLAT, ISOR, DELU, and SIMU. The final refinement was performed via modification of the structure factors for the electron densities in the solvent pore (2090 Å³, 26.9% of the total unit cell volume; 429 electrons correspond to ~11 DMF molecules per unit cell) using the

SQUEEZE option in PLATON.^{S5} Refinement of the structure converged at a final R1 = 0.0442 and wR2 = 0.1321 for 5905 reflections with $I > 2\sigma(I)$; R1 = 0.0545 and wR2 = 0.1386 for all 7566 reflections. The largest difference peak and hole were 0.785 and $-1.352 \text{ e} \cdot \text{Å}^{-3}$, respectively.

A summary of the crystallographic data is provided in Supplementary Table S1. CCDC 2000395-2000398 contains the supplementary crystallographic data for AgBTB, AgBTB-dpey, AgBTB-dpt, and AgBTB-bpy. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK.

III. Supplementary References

- S1. J. W. Shin, K. Eom, D. Moon, PAL BL2D-SMDC Program. J. Synchrotron Rad. 2016, 23, 369-373.
- S2. Z. Otwinowski, W. Minor, in *Methods in Enzymology*, Ed. C. W. Carter, Jr. and R. M. Sweet, Academic Press, New York, 1997, vol. 276, part A, pp. 307.
- S3. Rapid Auto software, R-Axis series, Cat. No. 9220B101, Rigaku Corporation.
- S4. SHELX program: G. M. Sheldrick, Acta Crystallogr. C. 2015, 71, 3-8.
- S5. PLATON program: A. L. Spek, Acta Crystallogr. C. 2015, 71, 9–18.

IV. Supplementary Table

Table S1. Crystal data and structure refinement for AgBTB, AgBTB-dpey, AgBTB-dpt and AgBTB-bpy.

	AgBTB	AgBTB-dpey	AgBTB-dpt	AgBTB-bpy
Empirical formula	$C_{216}H_{131.20}O_{53.60}Ag_{24}$	$C_{252.21}H_{144.14}N_{6.04}O_{48}Ag_{24}\\$	$C_{251.75}H_{143.83}N_{17.87}O_{48}Ag_{24}$	$C_{279.89}H_{171.11}N_{12.78}O_{48}Ag_{24}$
Formula weight	6172.88	6615.83	6775.73	7069.88
Temperature, K	298(2)	296(2)	173(2)	296(2)
Wavelength, Å	0.700	0.700	0.71073	0.650
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>I</i> 2/ <i>a</i>	<i>I</i> 2	$P2_{1}/c$	I2/a
Unit cell dimensions, Å and °	a = 34.285(7)	a = 34.592(7)	a = 34.512(7)	a = 33.950(7)
	b = 5.9340(12)	b = 6.2570(13)	b = 5.9589(12)	b = 6.0020(12)
	c = 39.220(18)	c = 35.505(18)	c = 38.939(19)	c = 39.546(18)
	$\beta = 104.56(3)$	$\beta = 107.21(3)$	$\beta = 104.48(3)$	$\beta = 105.22(3)$
Volume, Å ³	7723(4)	7341(4)	7754(5)	7776(4)
Z	1	1	1	1
Density (calculated), mg/m ³	1.327	1.497	1.451	1.510
Absorption coefficient, mm ⁻¹	1.452	1.533	1.537	1.191
F(000)	2984	3212	3291	3452
Crystal size, mm ³	0.17 x 0.11 x 0.02	0.06 x 0.05 x 0.02	0.17 x 0.11 x 0.07	0.08 x 0.07 x 0.02
θ range for data collection, $^\circ$	2.783 to 25.997	1.697 to 23.198.	3.048 to 27.490.	1.137 to 23.999
Index ranges	-41<=h<=38	-36<=h<=36	-44<=h<=44	-40<=h<=40
	-7<=k<=7	-7<=k<=7	-7<=k<=7	-7<=k<=7
	-49<=l<=49	-39<=l<=39	-50<=l<=50	-49<=l<=49
Reflections collected	23071	20422	61289	27369
Independent reflections	7571 [R(int) = 0.0931]	10393 [R(int) = 0.0381]	17170 [R(int) = 0.1775]	7566 [R(int) = 0.0250]
Completeness, % (°)	96.2 (theta = 24.835)	94 (theta = 23.198)	97.7 (theta = 25.242)	95 (theta = 22.955)
Max. and min. transmission	0.969 and 0.790	0.968 and 0.916	0.900 and 0.779	0.976 and 0.910
Data / restraints / parameters	7571 / 0 / 335	10393 / 152 / 752	17170 / 324 / 787	7566 / 0 / 433
Goodness-of-fit on F ²	0.905	0.982	1.246	1.07
Final R indices [I>2 σ (I)]	R1 = 0.0768	R1 = 0.0519	R1 = 0.1703	R1 = 0.0442
	wR2 = 0.2134	wR2 = 0.1420	wR2 = 0.3946	wR2 = 0.1321
R indices (all data)	R1 = 0.1264	R1 = 0.0739	R1 = 0.2670	R1 = 0.0545
	wR2 = 0.2533	wR2 = 0.1557	wR2 = 0.4501	wR2 = 0.1386
Absolute structure parameter	-	0.47(5)	-	-
Extinction coefficient	0.0013(2)	-	-	-
Largest diff. peak and hole, $e \cdot \mathring{A}^{-3}$	0.908 and -0.876	1.042 and –0.683 $^{\scriptscriptstyle 3}$	7.595 and -1.552	0.785 and -1.352



Fig. S1 Crystal structure of **AgBTB**. (a) A 3D network with 1D solvent channels along the crystallographic *b*-axis. (b) Three binding modes of the carboxylates of the 3-c BTB ligand. (c) The distorted square pyramidal coordination geometry of Ag2 and Ag3.



Fig. S2 The single crystals of **AgBTB** soaked in 10 mL of 30 μ M Nile red (NR) and methylene blue (MeB) EtOH solutions for 48 h. UV-vis spectra of various dye solutions with **AgBTB** in ethanol: methylene blue (MeB) and Nile Red (NR).



Fig. S3 Three dipyridyl linkers (dpey, dpt, and bpy) used for insertion into the framework of **AgBTB**. The lengths of the dipyridyl linkers (blue) with the corresponding inter-silver distances, including two Ag-N coordination bonds of ~2.4 Å (violet).



Fig. S4 The as-prepared and simulated PXRD patterns of AgBTB, AgBTB-dpey, AgBTB-dpey(40), AgBTB-dpt, AgBTB-dpt(40), AgBTB-bpy and AgBTB-bpy(40).



Fig. S5 The coordination geometries of the (a) dinuclear and (b) tetranuclear clusters of AgBTB-dpey.

Crystal structure of AgBTB-dpey. While the dpey-linkage between the dinuclear clusters reduced the inter-Ag distance by ~0.5 Å (from 14.7 Å in **AgBTB** to 14.2 Å in **AgBTB-dpey**), the dpey-linkage between the tetranuclear clusters induced a ~0.3 Å expansion of the inter-silver distance between dinuclear clusters (from 14.7 Å in **AgBTB** to 15.0 Å in **AgBTB-dpey**). This change from contraction to expansion of the inter-silver distances between the dinuclear clusters maintained the average channel dimension of **AgBTB-dpey** along the crystallographic (1 0 0) direction as similar to that of the corresponding channel dimension of **AgBTB**. In contrast, the dpey-linkage between the tetranuclear clusters (from 17.3 Å in **AgBTB** to 14.8 Å in **AgBTB-dpey**). The dpey-linkage between the dinuclear clusters

resulted in a ~1.5 Å contraction of the inter-silver distance between the tetranuclear clusters (from 17.3 Å in AgBTB to 15.8 Å in AgBTB-dpey). The alternating contractions of the channel dimensions between tetranuclear clusters resulted in an overall contraction of the framework structure along the crystallographic (0 0 1) direction. The anisotropic contractions of the solvent channels produced alternating inter-silver linkages between the dinuclear and tetranuclear clusters. Insertion of dpey linker resulted in an overall contraction of the solvent channel dimensions and subsequent ~5% contraction of the unit cell volume. Alternation of the two types of dpey linkages generated two 1D solvent channels. The first type of the 1D solvent channel with rectangular channel dimensions of $3.7 \times 11.6 \text{ Å}^2$, the type A channel, was generated via division of the 1D solvent channel in AgBTB by the dpey linkages between the dinuclear clusters. The other 1D solvent channel with rectangular channel dimensions of 3.8×9.8 Å², the type **B** channel, was generated via division of the same 1D solvent channel in **AgBTB** by the dpey linkages between the tetranuclear clusters. The linkage between the silver ions of the dinuclear clusters altered the coordination geometries of the two silver ions from an inverted symmetric 4,4-coordinate square-planar/square-planar structure to an asymmetric 3,4-coordinate square-planar/Tshaped triangular structure. The dpey linkage between tetranuclear clusters also changed the coordination geometries of the tetranuclear clusters from an inverted symmetric 5,5,5,5-coordinate all square-pyramidal structure to an asymmetric 6,5,5,5-coordinate distorted octahedral/squarepyramidal/square-pyramidal structure. Increased coordination number at the Ag2 ion (Ag2 is labeled as Ag3 in the single crystal structure of AgBTB-dpey because the asymmetric unit in **AgBTB-dpey** is doubled to that in **AgBTB**) of the tetranuclear cluster from 5 to 6 weakened the other silver-oxygen and silver-silver bonds. The different binding energies of the dpey linkers are reflected in the different Ag-N bond lengths at the two dpey linkage sites. The Ag2-N bond length at the squareplanar Ag(I) site of the dinuclear cluster is ~0.2 Å shorter than the Ag3-N bond length at the distorted octahedral Ag(I) site in the tetranuclear cluster.



Fig. S6 Comparison of the binding modes of (a) dpey and (b) dpt between dinuclear clusters across the solvent channels in **AgBTB-dpey** and **AgBTB-dpt**, respectively.

Crystal structure of AgBTB-dpt. The dpt linkers in **AgBTB-dpt** interconnect the second shortest dinuclear silver clusters across the solvent channel, without any significant structural rearrangement. The dpt linkage unevenly partitioned the original 1D channel into two smaller 1D rectangular channels with sizes of 3.6×11.9 Å² (channel C) and 5.2×12.3 Å² (channel D).



Fig. S7 The binding of a bpy linker between two kinds of silver clusters in AgBTB-bpy.

Crystal structure of AgBTB-bpy. The insertion of bpy linkers occurs between the dinuclear and tetranuclear silver clusters without significant framework rearrangement. The dimensions of the new 1D rectangular channel **E** in **AgBTB-bpy** is 5.2×12.6 Å². The coordination geometry of Ag1 at the dinuclear cluster is similar to that observed in **AgBTB**. However, the Ag1-N bond distance is much shorter than that of Ag1-O in **AgBTB**. In contrast, the Ag2-N bond distance at the tetranuclear cluster in **AgBTB-bpy** is slightly longer than the corresponding bond distance in **AgBTB-dpey**.



Fig. S8 The ¹H NMR spectrum of AgBTB-dpey digested in DMSO-*d*₆ with a drop of aqueous DCl.



Fig. S9 The ¹H NMR spectrum of AgBTB-dpt digested in DMSO-*d*₆ with a drop of aqueous DCl.



Fig. S10 The ¹H NMR spectrum of **AgBTB-bpy** digested in DMSO-*d*₆ with a drop of aqueous DCl.



Fig. S11 The amounts of dipyridyl linkers in AgBTB-dpey(x), AgBTB-dpt(x), and AgBTB-bpy(x) after soaking in x mL of either 1 or 2 mM dpey and dpt MC solutions.



Fig. S12 (a) The N₂ sorption isotherms of activated **AgBTB (AgBTB-a)** at 77 K. (b) The CO₂ sorption isotherms of **AgBTB-a** at 195, 273, and 298 K (Filled circles: adsorption; Empty circles: desorption).



Fig. S13 The CO₂ sorption isotherms of **AgBTB-dpey(40)a** and **AgBTB-dpey(10)a** at 273 and 298 K (Filled squares and triangles: adsorption; Empty squares and triangles: desorption).



Fig. S14 The N₂ sorption isotherms of **AgBTB-dpt(40)a** and **AgBTB-dpt(10)a** at 77 K (Filled circles: adsorption; Empty circles: desorption).



Fig. S15 The CO₂ sorption isotherms of **AgBTB-dpt(40)a** and **AgBTB-dpt(10)a** at 273 and 298 K (Filled squares and triangles: adsorption; Empty squares and triangles: desorption).



Fig. S16 The N₂ sorption isotherms of **AgBTB-bpy(40)a** and **AgBTB-bpy(10)a** at 77 K (Filled circles: adsorption; Empty circles: desorption).



Fig. S17 The CO₂ sorption isotherms of **AgBTB-bpy(40)a** and **AgBTB-bpy(10)a** at 273 and 298 K (Filled squares and triangles: adsorption; Empty squares and triangles: desorption).