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<Supplementary Information>

Solvent-mediated framework flexibility of interdigitated 2D layered metal-organic frameworks

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Experimental section

General procedures

All reagents were purchased from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) data were recorded using a Bruker D2 Phaser automated diffractometer at room temperature, with a step size of $2\theta = 0.02°$. Variable temperature ^1H nuclear magnetic resonance (NMR) spectra were recorded using a 400 MHz FT-NMR spectrometer at the UNIST Central Research Facilities. Thermogravimetric analysis (TGA) was performed using a STD Q-600 series instrument from TA Instruments at a heating rate of 10 °C min^{-1} under flowing N_2. The sample was dried before the TGA measurement using flowing N_2 for 60 min. All the gas sorption isotherms were measured using a BELSORP-max (BEL Japan, Inc.) adsorption system employing a standard volumetric technique up to saturation pressure. The N_2 (purity of 99.999%) sorption isotherms were monitored at 77 K. The CO_2 (purity of 99.999%) sorption isotherms were measured at 195 K.

Synthesis of the 3,3'-((3,4-dioxocyclobut-1-ene-1,2-diyl)bis(azanediyl))dibenzoic acid (H_2dbda) ligand

3,3'-((3,4-Dioxocyclobut-1-ene-1,2-diyl)bis(azanediyl))dibenzoic acid (H_2dbda) was synthesized according to the reported procedure with minor modifications.[S1] 3-Aminobenzoic acid (5.76 g, 42.0 mmol), $Zn(CF_3SO_3)_2$ (1.45 g, 4.00 mmol), and 3,4-diethoxy-3-cyclobutene-1,2-dione (2.5 mL, 17 mmol) were added into toluene (190 mL) and *N*-methyl-2-pyrrolidone (10 mL). After refluxing at 100 °C for 24 h under N_2 atmosphere, a yellowish green precipitate was harvested by filtration and washed in boiling MeOH (90 mL) for 1 h. The yellowish green precipitate was then filtered and washed with MeOH (50 mL) again. After dissolving the precipitate (~ 110 mg) in DMA (20 mL) at 120 °C, MeOH (20 mL) was added to the solution. The solution, kept at −18 °C for 1 d, produced yellow precipitate and the yellow precipitate was removed from the solution by filtration. The addition of water (40 mL) to the filtrate yielded the yellowish pink product. The product was filtered, washed with MeOH (50 mL), and dried at 80 °C for 12 h. Yield: 4.29 g (72%). ^{1}H NMR (400 MHz, DMSO-d_6) [δ, ppm]:10.09 (s, 2H), 10.11 (s, 2H), 7.99 (s, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) [δ, ppm]: 182.48, 167.31, 166.11, 139.27, 132.48, 130.14, 124.43, 123.08, 119.64. ESI-MS (m/z): $[M]^-$ calc. for $Hdbda^-$ ($[C_{18}H_{11}N_2O_6]^-$): 351.0617; found: 351.0622.

Preparation of MOFs

[Cd(dbda)(bipy)]·2DMA·2H$_2$O (**1**). A mixture of H_2dbda (18 mg, 0.051 mmol), 4,4'-bipyridine (bipy, 9.0 mg, 0.058 mmol) and $Cd(NO_3)_2\cdot4H_2O$ (17 mg, 0.055 mmol) was dissolved in DMA/water mixed solvent (15 mL, 2:1 volume ratio) in a 20 mL screw capped vial. The solution was placed in an oven at 70 °C for two weeks and produced colorless block-shaped crystals (**1**). After cooling the solution to ambient temperature, the crystals were quickly collected by filtration and air-dried. Yield: 27.2 mg (45%). The number of DMA and water molecules in **1** was determined based on the single crystal structure and/or the ^{1}H NMR spectrum of the crystals digested in DMSO-d_6/DCl mixed solvent.

[Cd(dbda)(bipy)]·1.74DMA (**1a**). Activated **1** (**1a)** was prepared by placing **1** in a vacuum at 20 °C for 24 h. The number of DMA molecules in **1a** was determined based on the ^{1}H NMR spectrum of the crystals digested in DMSO-d_6/DCl mixed solvent.

[Cd(dbda)(bipy)]·DMA (**2**). Method A. Single crystals of **2** were prepared by heating **1** to 150 °C at a heating rate of 10 °C min^{-1} under flowing N_2 and then aging for 1 h, followed by exposure to ambient conditions. Method B. **2** can also be prepared by heating **1** at 130 °C for

24 h under vacuum, and then exposing it to ambient conditions. The number of DMA molecules in **2** was determined based on the single crystal structure and/or the ^{1}H NMR spectrum of the crystals digested in DMSO-d$_6$/DCl mixed solvent.

[Cd(dbda)(bipy)]·0.83DMA (**2a**). Activated **2** (**2a)** was prepared by heating **1** at 130 °C for 24 h under vacuum. The number of DMA molecules in **2a** was determined based on the ^{1}H NMR spectrum of the crystals digested in DMSO-d$_6$/DCl mixed solvent.

[Cd(dbda)(bipy)]·H$_2$O (**3**). Method A. Single crystals of **3** were prepared by heating **1** to 275 °C at a heating rate of 10 °C min^{-1} under flowing N$_2$ and then aging for 1 h, followed by exposure to ambient conditions. The number of DMA molecules in **3** was determined based on the ^{1}H NMR spectrum of the MOF crystal digested in DMSO-d$_6$/DCl mixed solvent at ambient conditions. Method B. **3** can also be prepared by heating **1** at 180 °C for 24 h under vacuum, and then exposing it to ambient conditions.

[Cd(dbda)(bipy)] (**3a**). Activated **3** (**3a)** was prepared by heating **1** at 180 °C for 24 h under vacuum.

Crystallographic data collection and refinement of the structures

Single crystals of **1**, **2**, and **3** were coated with Paratone-N oil and the diffraction data were measured at 173 K with Mo Kα radiation on an X-ray diffraction camera system using an imaging plate equipped with a graphite crystal incident beam monochromator. RapidAuto software[S2] was used for data collection and data processing. The structures were solved by either the direct method or the charge flip method and were refined by the full-matrix least-squares calculation with the SHELX software package.[S3]

1, [Cd(dbda)(bipy)]·2DMA·$2H_2O$. A colorless, block shaped crystal, 0.250 × 0.150 × 0.085 mm^3 was used for data collection. Crystal data for $C_{36}H_{40}N_6O_{10}Cd$ (fw = 829.14 $g\cdot mol^{-1}$): triclinic, space group P-1, a = 10.759(2) Å, b = 11.638(2) Å, c = 16.132(3) Å, α = 97.95(3)°, β = 91.80(3)°, γ = 108.00(3)°, V = 1896.6(7) $Å^3$, Z = 2, μ (λ = 0.71073 Å) = 0.639 mm^{-1}, 18,283 reflections were collected, of which 8,446 were unique (R_{int} = 0.0187). One Cd ion, $dbda^{2-}$, one bipy, two DMA molecules, and two water molecules are observed in an asymmetric unit. All non-hydrogen atoms are refined anisotropically; the hydrogen atoms were assigned isotropic displacement coefficients, U(H) = 1.2U (C and N) and 1.5U (C_{methyl}), and their coordinates were allowed to ride on their respective atoms. The cyclobut-3-ene-1,2-dione group of the dbda ligand is statistically disordered and the geometries are restrained to be the same using SAME command. The hydrogen atoms of the water molecules are not included in the least-square refinement. Refinement of the structure converged at a final $R1$ = 0.0430 and $wR2$ = 0.1064 for 7,389 reflections with $I > 2\sigma(I)$; $R1$ = 0.0519 and $wR2$ = 0.1112 for all 8,446 reflections. The largest difference peak and hole were 1.372 and -0.994 $e\cdot Å^{-3}$, respectively.

2, [Cd(dbda)(bipy)]·DMA. A colorless, rod shaped crystal, 0.123 × 0.054 × 0.030 mm^3 was used for data collection. Crystal data for $C_{32}H_{27}N_5O_7Cd$ (fw = 705.98 g·mol^{-1}): triclinic, space group P-1, a = 10.421(2) Å, b = 11.613(2) Å, c = 14.115(3) Å, α = 80.06(3)°, β = 75.45(3)°, γ = 69.73(3)°, V = 1544.1(7) Å^3, Z = 2, μ (λ = 0.71073 Å) = 0.763 mm^{-1}, 15,200 reflections were collected, of which 7,053 were unique (R_{int} = 0.1434). One Cd ion, one dbda^{2-}, one bipy, and one DMA molecule are observed in an asymmetric unit. All non-hydrogen atoms are refined anisotropically; the hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U (C and N) and 1.5U (C_{methyl}), and their coordinates were allowed to ride on their respective atoms. Refinement of the structure converged at a final $R1$ = 0.1051 and $wR2$ = 0.1341 for 3,958 reflections with $I > 2\sigma(I)$; $R1$ = 0.1890 and $wR2$ = 0.1589 for all 7,053 reflections. The largest difference peak and hole were 0.774 and -0.582 e·Å^{-3}, respectively.

3, [Cd(dbda)(bipy)]·H_2O. A pale yellow, plate-shaped crystal, 0.087 × 0.055 × 0.024 mm^3 was used for data collection. Crystal data for $C_{28}H_{20}N_4O_7Cd$ (fw = 636.88 g·mol^{-1}): monoclinic, space group P-1, a = 8.574(2) Å, b = 10.835(2) Å, c = 15.149(3) Å, α = 99.67(3)°, β = 97.74(3)°, γ = 107.38(3)°, V = 1298.0(5) Å^3, Z = 2, μ (λ = 0.71073 Å) = 0.897 mm^{-1}, 9,859 reflections were collected, of which 4,555 were unique (R_{int} = 0.2626). One Cd ion, one dbda^{2-}, one bipy and one water molecule are observed in an asymmetric unit. All non-hydrogen atoms are refined anisotropically; the hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U (C and N), and their coordinates were allowed to ride on their respective atoms. Highly anisotropic displacement parameters of several ligand atoms are restrained using the ISOR command. The hydrogen atoms of the water molecule are not included in the least-square refinement. Refinement of the structure converged at a final $R1$ = 0.1972 and $wR2$ = 0.3528 for 2,079 reflections with $I > 2\sigma(I)$; $R1$ = 0.3168 and *wR*2 = 0.4200 for all 4,555 reflections. The largest difference peak and hole were 2.036 and –0.860 e·Å^{-3}, respectively

A summary of the crystallographic data is provided in the Supplementary Tables S4–S6. CCDC 2061490–2061492 contains the supplementary crystallographic data for **1**, **2**, and **3**. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Variable temperature PXRD

Variable temperature PXRD (VT-PXRD) patterns were recorded at the BL2D SMC beamline of the Pohang Accelerator Laboratory, Korea. Crystalline samples were ground in an agate mortar and packed in a capillary tube (0.3 mm diameter). Debye−Scherrer diffraction data were collected on a Rayonix MX225HS CCD detector with a fixed wavelength (λ = 1.00000 Å) and an exposure of 30 s. For in situ heating, the sample tube was attached to a custom-built housing equipped with a vacuum line and temperature-controlled stream of nitrogen gas. It was allowed for at least 5 min at the designated temperature before recording the diffraction patterns. The PAL BL2D-SMDC program[S4] was used for data collection, and the Fit2D program[S5] was used to convert the two-dimensional (2D) to one-dimensional (1D) patterns.

Table S1 π–π stacking, CH–π interactions, and close contacts (Å) in **1**, **2**, and **3**.[S6]

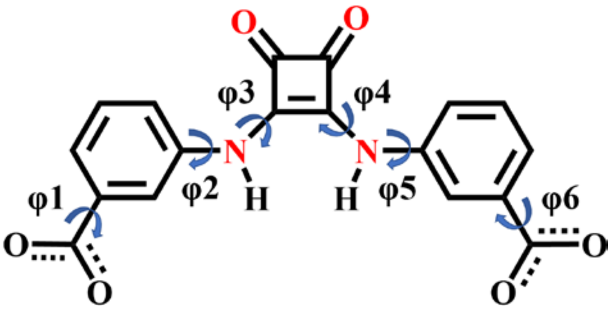
2D MOF	group pair	atom pair	distance	number and type of interactions
1	phenyl···phenyl	C2···C12	3.423(1)	two π-π interactions
2	phenyl···squaramide	C10···C17	3.386(1)	two π-π interactions
3	phenyl···squaramide	C5···C18 C6···C18	3.236(1) 3.371(1)	two π-π interactions
	phenyl···pyridyl	C13···C21 C13···C25 C13···C25	3.367(1) 3.495(1) 3.411(1)	one π-π interaction
	phenyl···phenyl	C13···O6 C13–H13···O6	3.271(1) 2.575(1)	one CH-π interaction

Table S2 Hydrogen bonding interactions (Å and °) of **1**, **2**, and **3**.[S7]

2D MOF	layer pair	atom pair	d(D-H)	d(H···A)	d(D···A)	<(DHA)
1	within 1D chain	N1–H1···O1D	0.88	2.02	2.888(5)	168.9
		N2–H2···O1D	0.88	2.00	2.864(5)	168.3
	between the adjacent 2D layers	O1W–H1W···O2#1	0.85(2)	2.14(3)	2.962(5)	162(8)
		O1W···O2D#2			3.113(2)	
		O1W···O2D#3			3.204(2)	
	between the next adjacent 2D layers	O2W···O51#2			2.84(3)	
		O2W···O61#4			2.64(13)	
		O2W···O52#2			3.04(4)	
		O2W···O62#4			2.75(11)	
2	within 1D chain	N1–H1···O1D#5	0.86	1.99	2.827(1)	162.9
		N2–H2···O1D#5	0.86	2.12	2.955(1)	162.4
3	between the adjacent 2D layers	N1–H1···O1S	0.88	2.03	2.90(3)	168.8
		N2–H2···O1S	0.88	2.14	2.96(3)	155.8
		O1S–H1···O5#6	0.84(2)	2.08(16)	2.86(3)	151(35)
		O1S–H1···O1#7	0.84(2)	1.90(7)	2.73(3)	171(39)

#1 1-x,1-y,1-z; #2 x,1+y,z; #3 1-x,1-y,2-z; #4 -x,1-y,1-z; #5 x,-1+y,1+z; #6 x+1,y,z; #7 -x+1,-y,-z+1

Table S3 Torsional angles (°) of dbda in **1**, **2** and **3**.



2D MOF	φ1	φ2	φ3	φ4	φ5	φ6
1	1.803	-177.0	179.6	10.19	173.9	-177.0
2	40.31	153.0	165.0	-9.6	-178.1	-162.5
3	41.13	-2.6	169.7	24.24	-62.1	177.9

Table S4 Crystal data and structure refinement for **1**.

Empirical formula	$C_{36}H_{40}N_6O_{10}Cd$	
Formula weight	829.14	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.759(2) Å	α = 97.95(3)°
	b = 11.638(2) Å	β = 91.80(3)°
	c = 16.132(3) Å	γ = 108.00(3)°
Volume	1896.6(7) Å^3	
Z	2	
Density (calculated)	1.452 mg/m^3	
Absorption coefficient	0.639 mm^{-1}	
F(000)	862	
Crystal size	0.250 × 0.150 × 0.085 mm^3	
Theta range for data collection	3.119 to 27.448°.	
Index ranges	-13<=h<=12, -15<=k<=15, -20<=l<=20	
Reflections collected	18283	
Independent reflections	8446 [R(int) = 0.0187]	
Completeness to theta = 25.242°	98.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8446 / 30 / 520	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.1064	
R indices (all data)	R1 = 0.0519, wR2 = 0.1112	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.372 and -0.994 e.Å^{-3}	

Table S5 Crystal data and structure refinement for **2**.

Empirical formula	$C_{32}H_{27}N_5O_7Cd$	
Formula weight	705.98	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 10.421(2) Å	α = 80.06(3)°
	b = 11.613(2) Å	β = 75.45(3)°
	c = 14.115(3) Å	γ = 69.73(3)°
Volume	1544.1(7) $Å^3$	
Z	2	
Density (calculated)	1.518 mg/m^3	
Absorption coefficient	0.763 mm^{-1}	
F(000)	716	
Crystal size	0.123 × 0.054 × 0.030 mm^3	
Theta range for data collection	2.289 to 27.484°.	
Index ranges	-13<=h<=13, -15<=k<=14, -17<=l<=18	
Reflections collected	15200	
Independent reflections	7053 [R(int) = 0.1434]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.970 and 0.331	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7053 / 0 / 406	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.1051, wR2 = 0.1341	
R indices (all data)	R1 = 0.1890, wR2 = 0.1589	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.774 and -0.582 $e·Å^{-3}$	

Table S6 Crystal data and structure refinement for **3**.

Empirical formula	$C_{28}H_{20}N_4O_7Cd$	
Formula weight	636.88	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 8.5738(17) Å	α = 99.67(3)°
	b = 10.835(2) Å	β = 97.74(3)°
	c = 15.149(3) Å	γ = 107.38(3)°
Volume	1298.0(5) Å^3	
Z	2	
Density (calculated)	1.630 mg/m^3	
Absorption coefficient	0.897 mm^{-1}	
F(000)	640	
Crystal size	0.087 × 0.055 × 0.024 mm^3	
Theta range for data collection	2.019 to 24.999°.	
Index ranges	-10<=h<=10, -12<=k<=12, -17<=l<=17	
Reflections collected	9859	
Independent reflections	4555 [R(int) = 0.2626]	
Completeness to theta = 24.999°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.976 and 0.012	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4555 / 44 / 367	
Goodness-of-fit on F^2	1.137	
Final R indices [I>2sigma(I)]	R1 = 0.1972, wR2 = 0.3528	
R indices (all data)	R1 = 0.3168, wR2 = 0.4200	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.036 and -0.860 e·Å^{-3}	

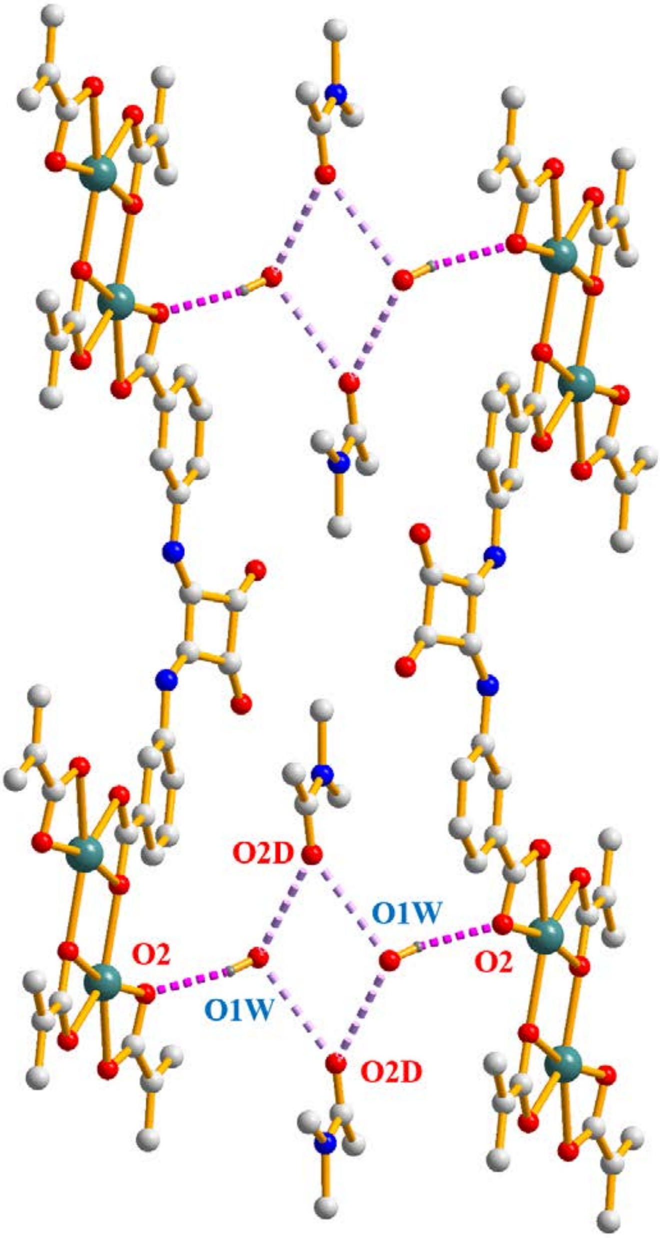


Fig. S1 (Potential) hydrogen bonding interactions between the adjacent interdigitated layers of **1**. OH···O hydrogen bonding and O···O close contacts are represented by pink and purple dotted lines, respectively. The minor part of the statistically disordered squaramide residue is omitted for clarity.

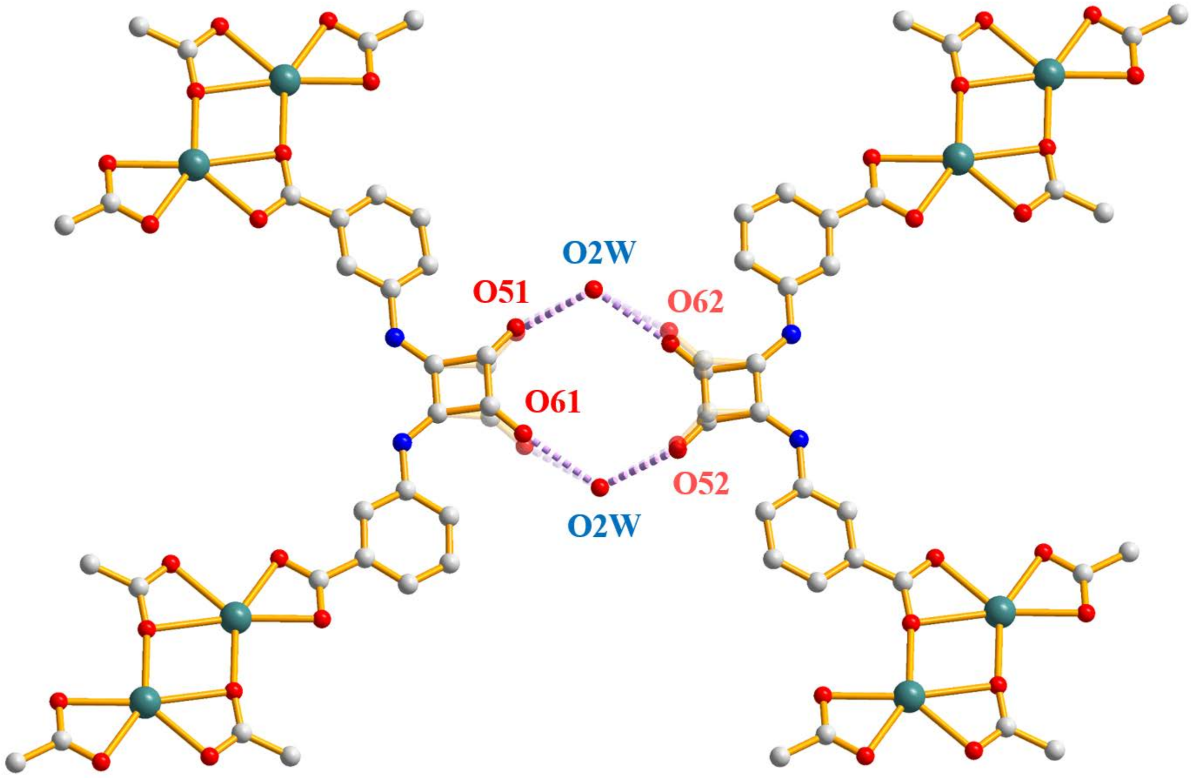


Fig. S2 (Potential) hydrogen bonding interactions between the next adjacent interdigitated layers of **1**. O···O close contacts are represented by purple dotted lines. The minor part of the statistically disordered squaramide residue is represented in partial transparency.

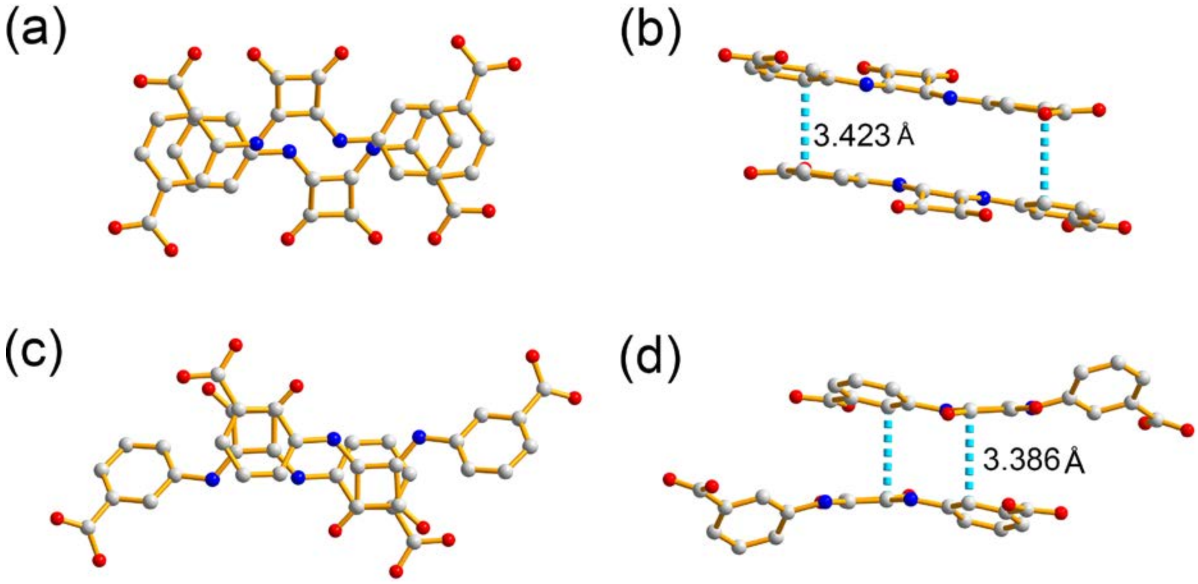


Fig. S3 π–π stacking interactions between 2D layers of (a, b) **1** and (c, d) **2** viewed approximately along the stacking direction and perpendicular to the stacking direction, respectively. The minor part of the statistically disordered squaramide residue is omitted for clarity.

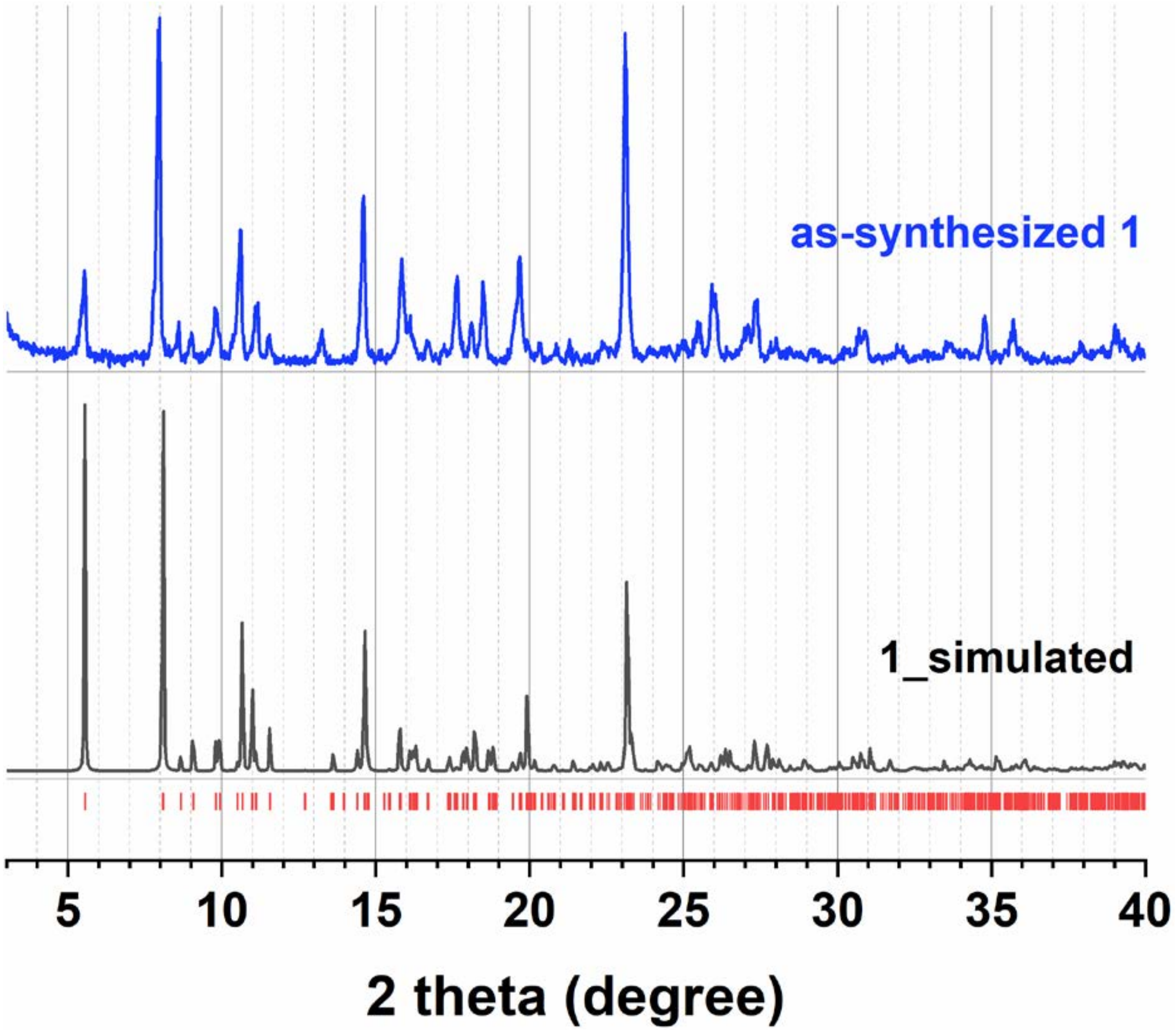


Fig. S4 Comparison of the observed and simulated PXRD pattern of **1**.

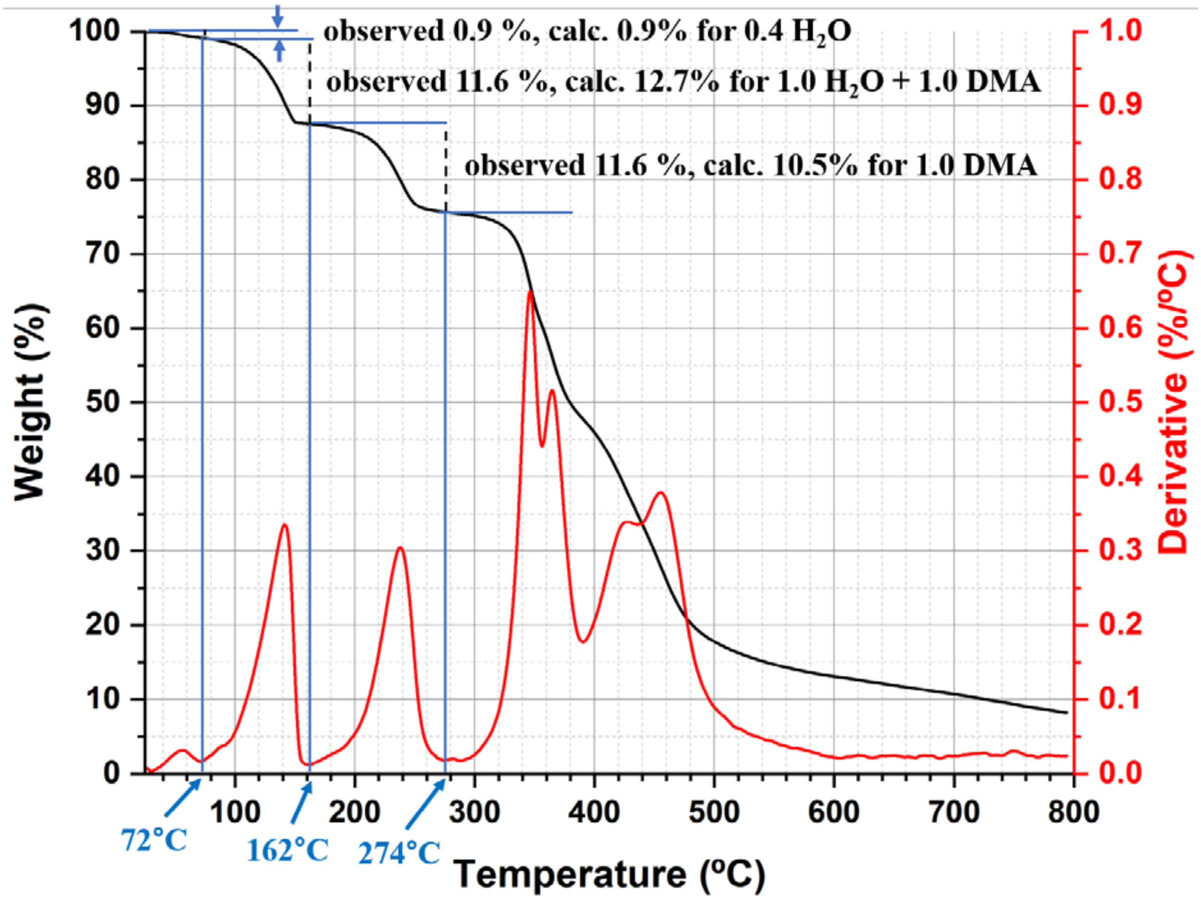


Fig. S5 TGA of **1** at a heating rate of 10 °C min^{-1} under flowing N_2.

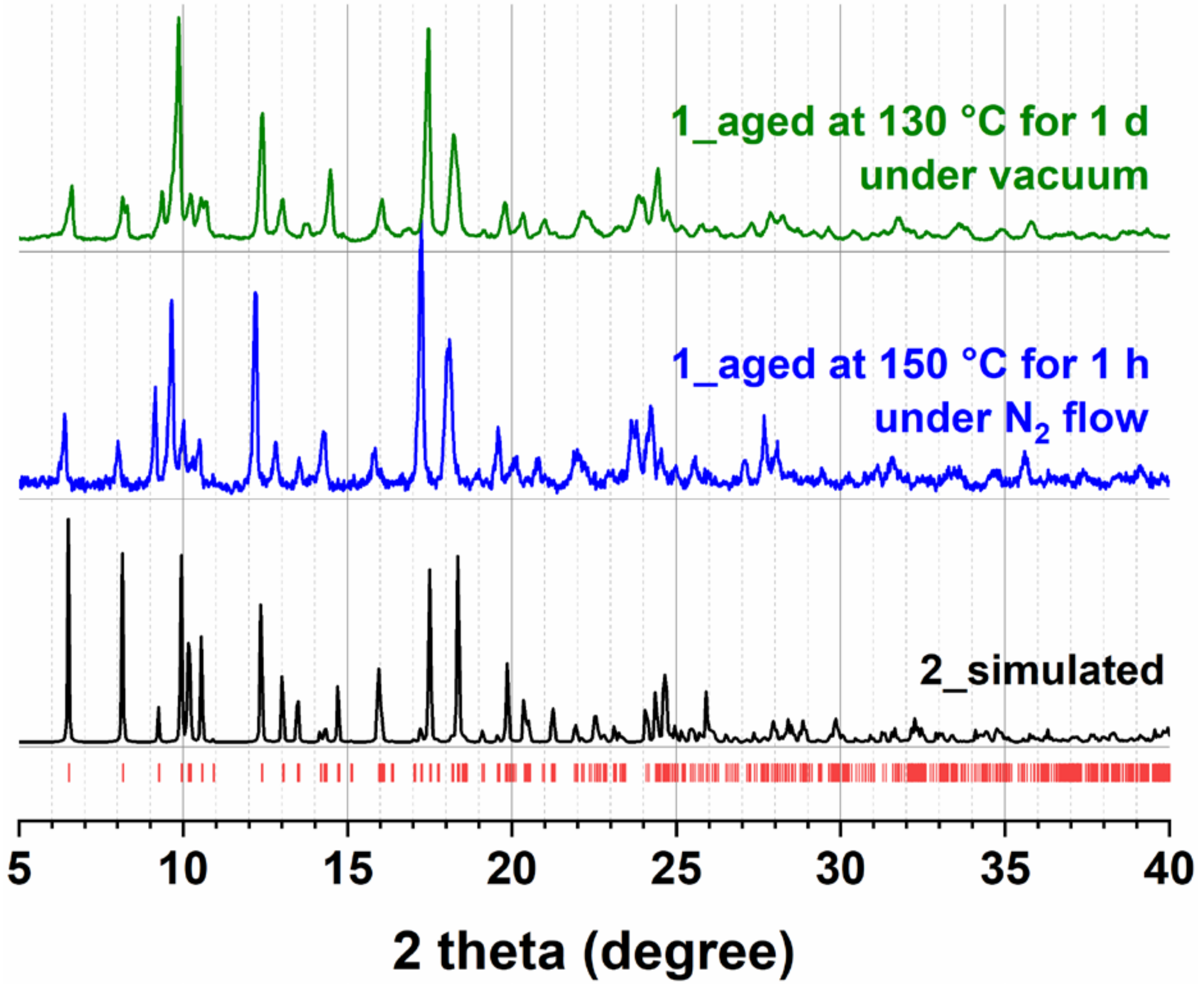


Fig. S6 Comparison of the PXRD patterns of **2** obtained by aging **1** either at 150 °C for 1 h under flowing N_2 or 130 °C for 1 d under vacuum.

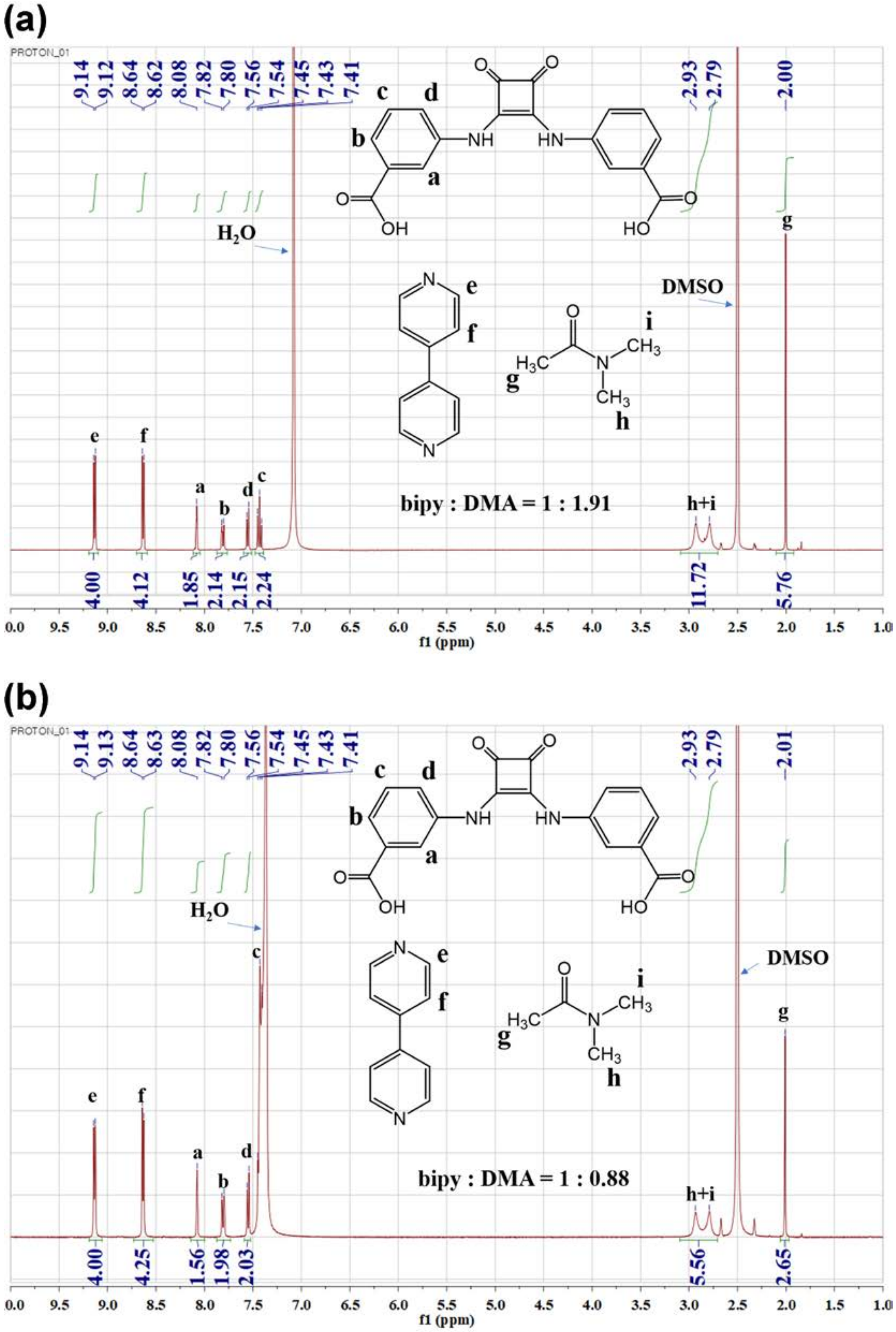


Fig. S7 ^1H NMR spectra of (a) **1** and (b) **2**.

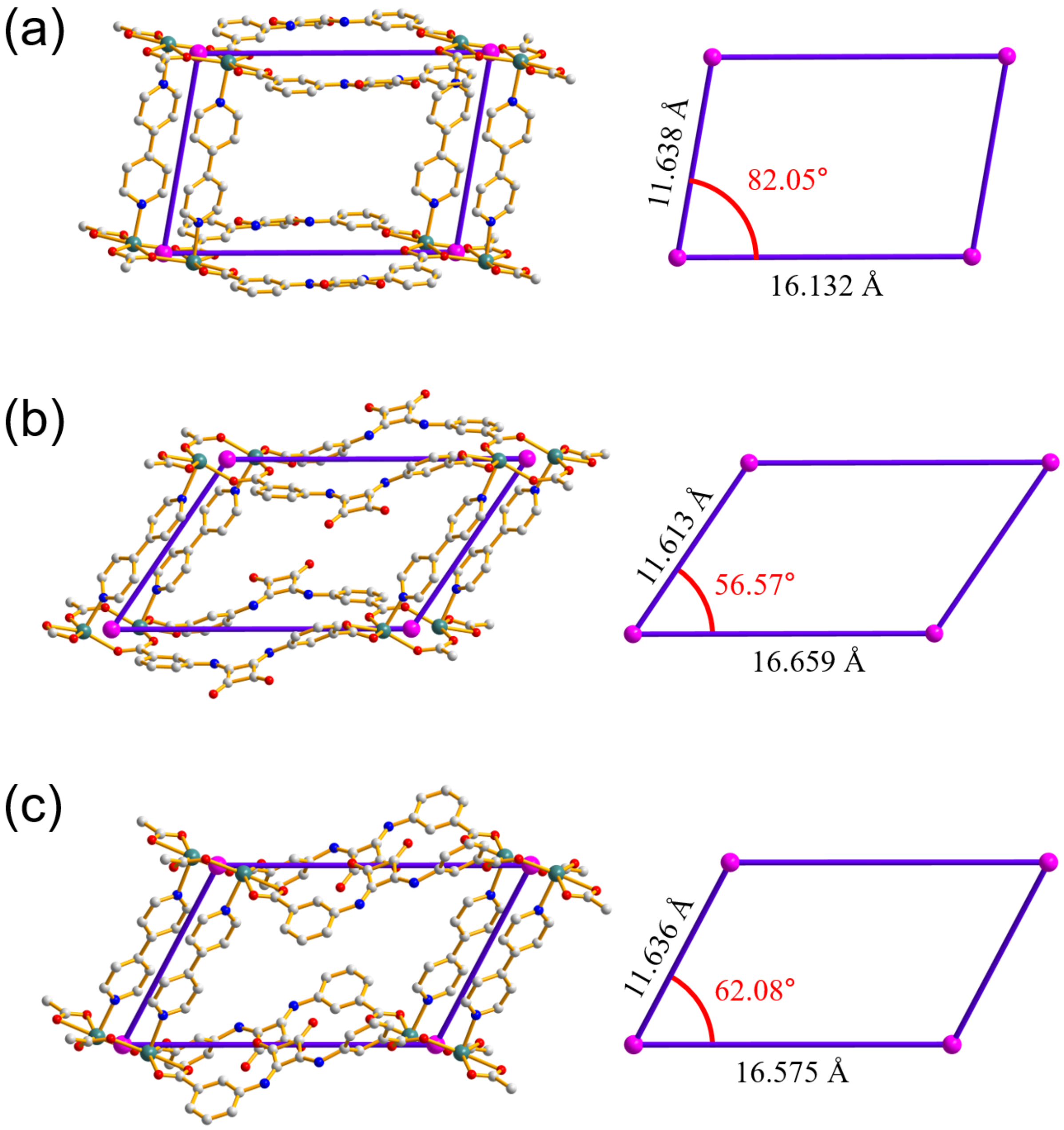


Fig. S8 2D layers of (a) **1**, (b) **2**, and (c) **3** with **sql** net topology and inter-cluster distances and angles, where the parallelograms consist of four dinuclear $Cd_2(COO)_4$ secondary building units (pink) doubly interconnected by both dbda ligands and two bipy linkers.

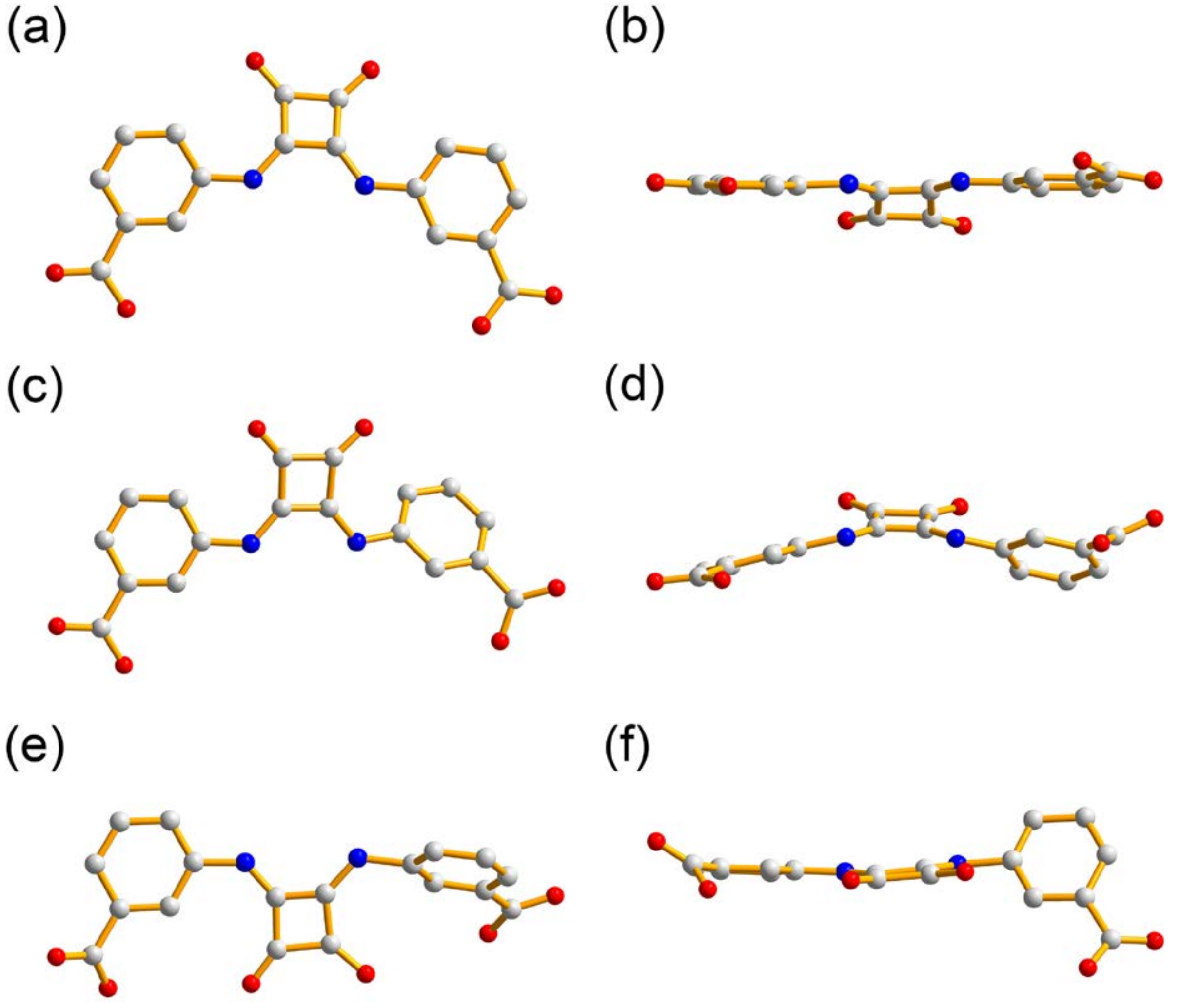


Fig. S9 Conformations of dbda ligand in (a, b) **1**, (c, d) **2**, and (e, f) **3** viewed approximately perpendicular to and along one of the phenyl groups of the ligand.

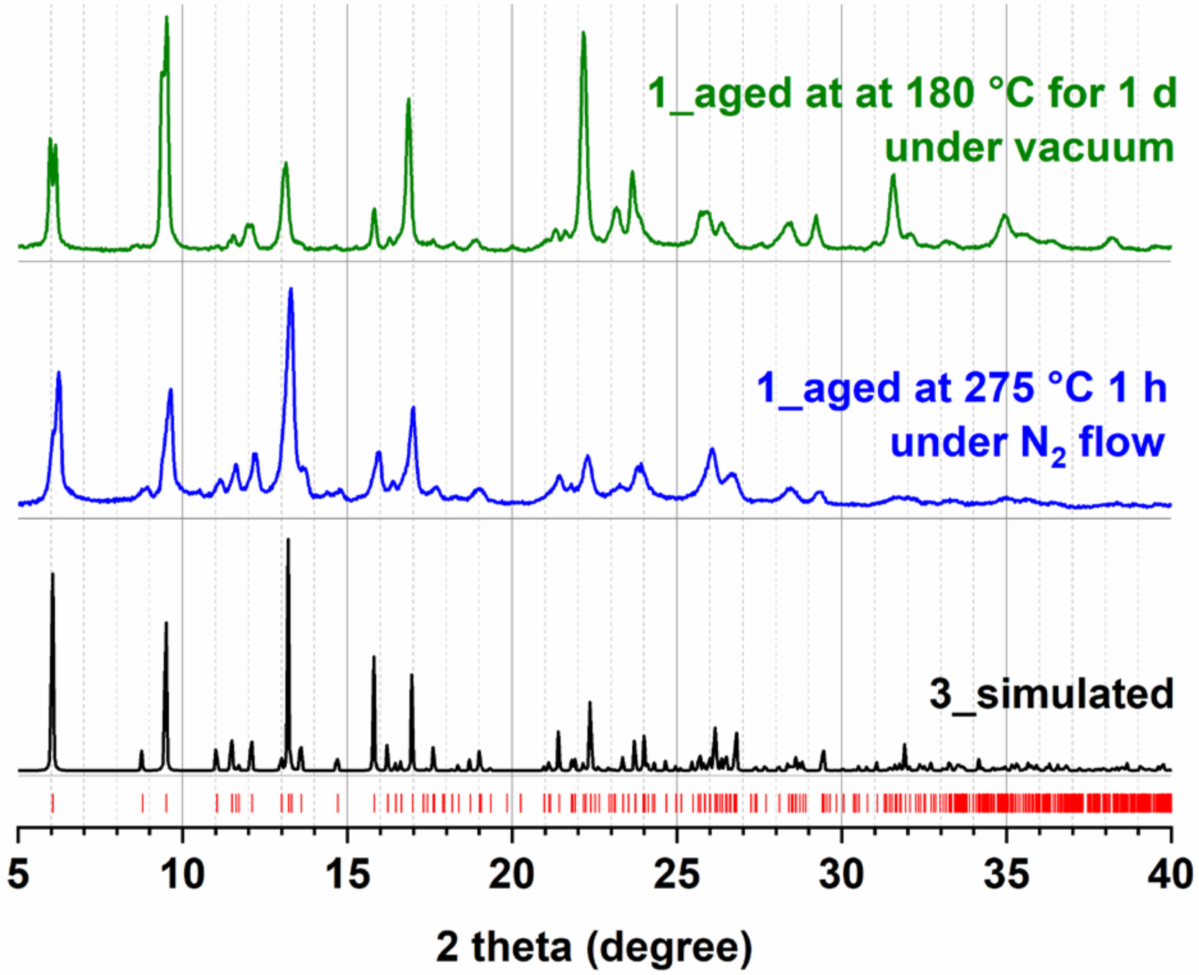


Fig. S10 Comparison of the PXRD patterns of **3** obtained by aging **1** either at 275 °C for 1 h under flowing N_2 or 180 °C for 1 d under vacuum.

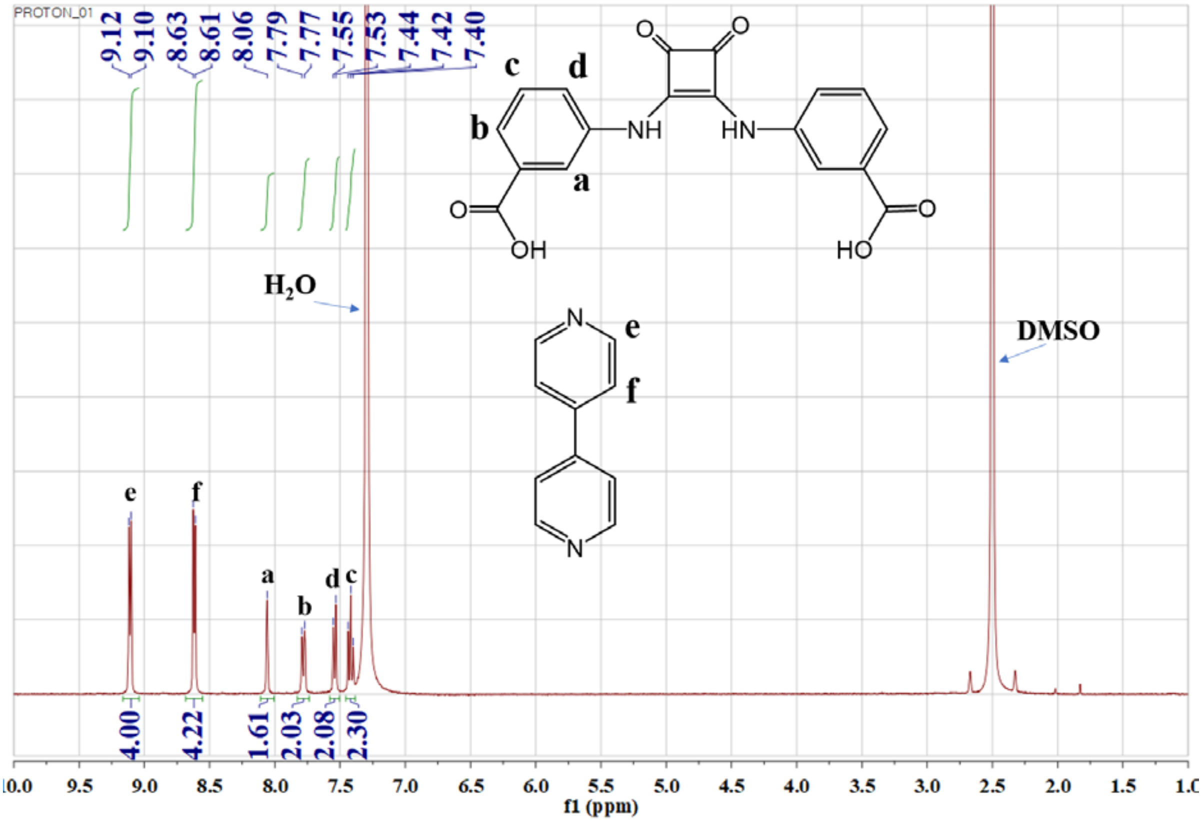


Fig. S11 ^{1}H NMR spectrum of **3**.

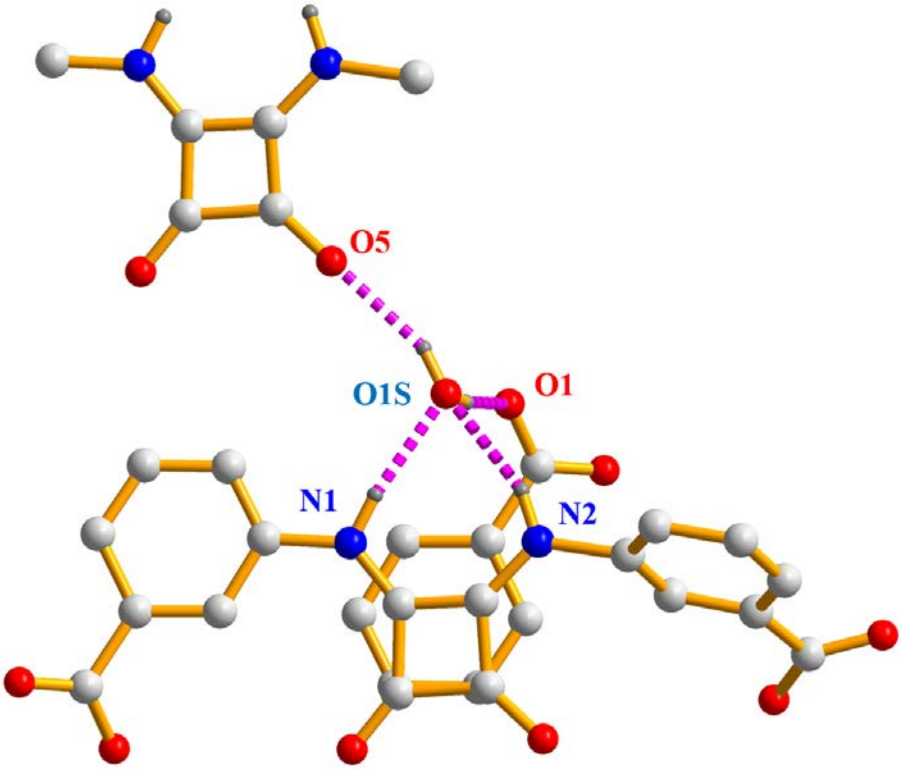


Fig. S12 Hydrogen bonding interactions involving a water molecule entrapped in the framework of **3**. OH (or NH)···O hydrogen bonding contacts are represented by pink dotted lines.

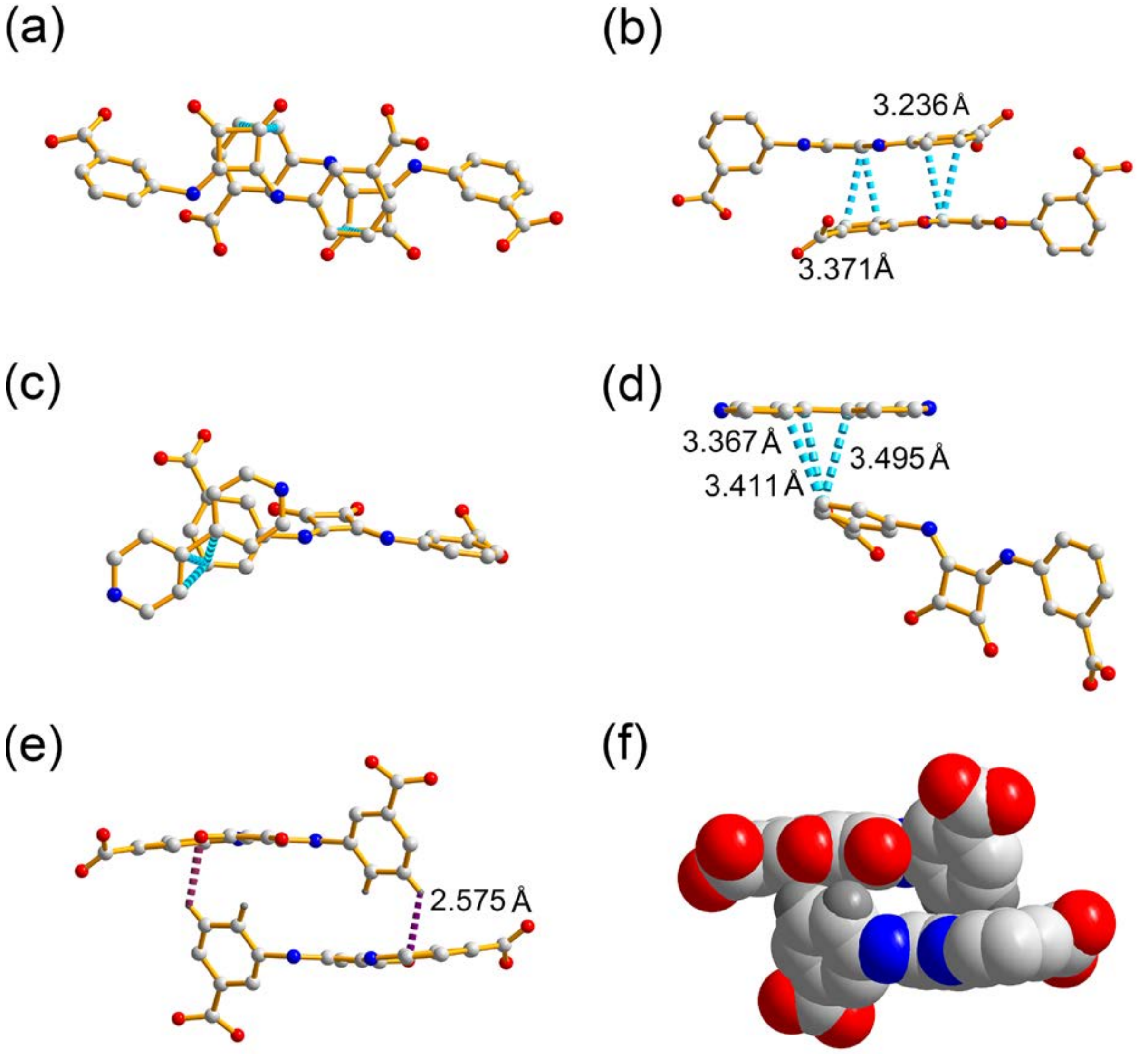


Fig. S13 π–π stacking interaction between phenyl and squaramide groups of **3** viewed approximately (a) along the stacking directions and (b) perpendicular to the stacking directions. The π–π stacking interaction between phenyl and pyridyl groups of **3** viewed approximately (c) along the stacking directions and (d) perpendicular to the stacking directions. The CH–π interaction between phenyl groups of **3** in (e) ball-and-stick and (f) CPK models.

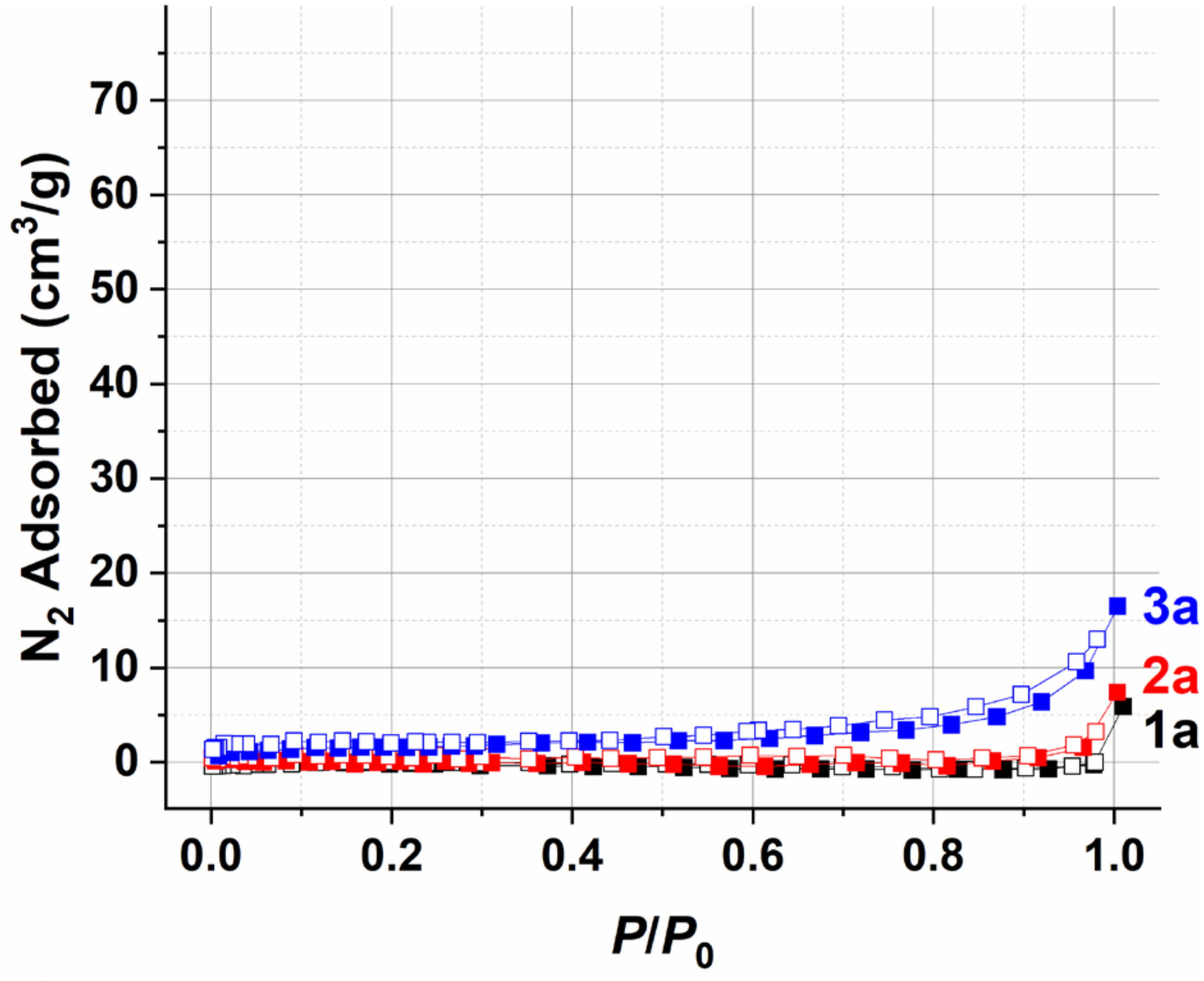


Fig. S14 N_2 adsorption isotherms (filled squares) and desorption isotherms (open squares) of **1a**, **2a**, and **3a** at 77 K.

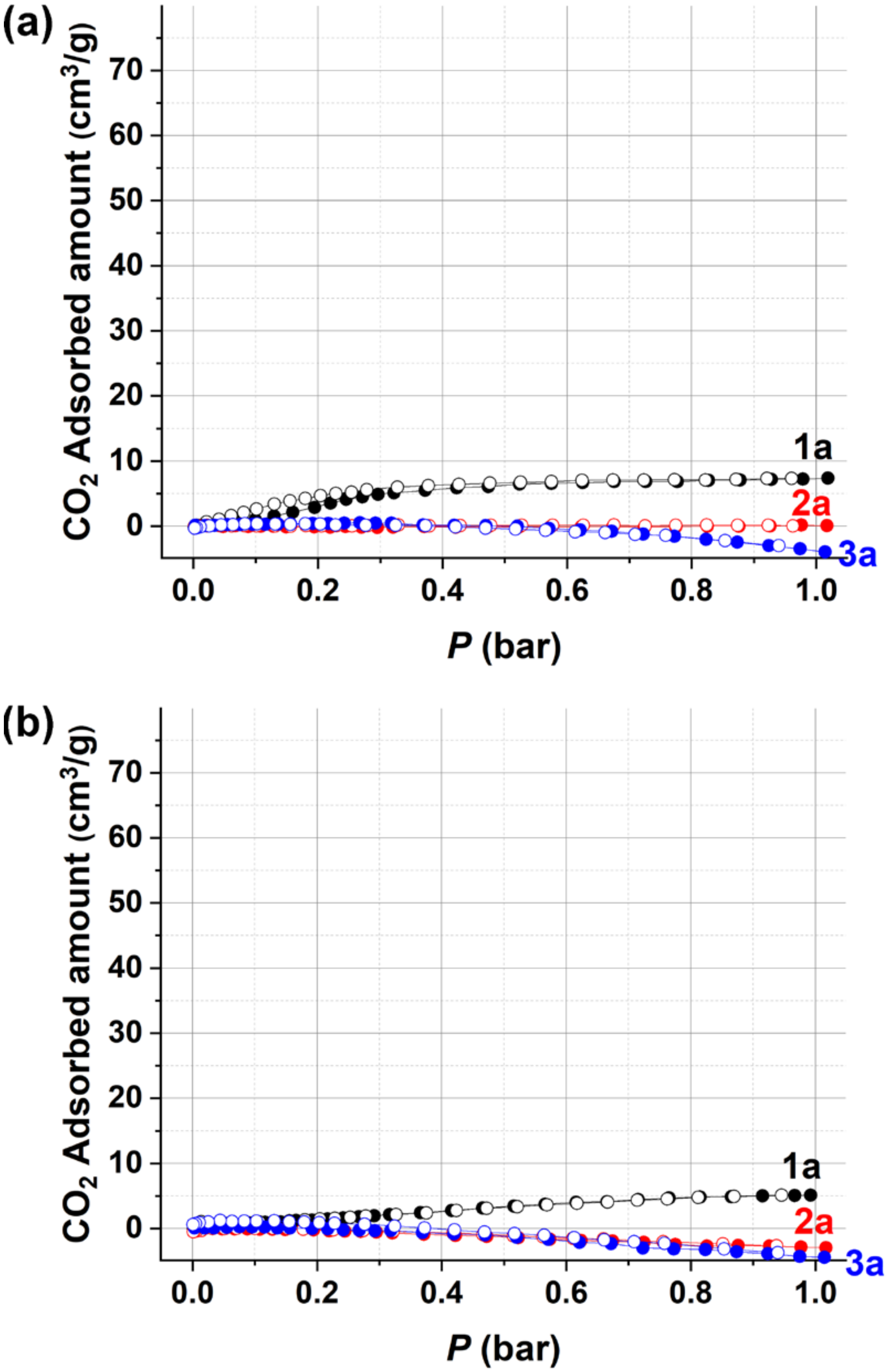


Fig. S15 CO_2 adsorption isotherms (filled circles) and desorption isotherms (open circles) of **1a**, **2a**, and **3a** at (a) 298 K and (b) 323 K.

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