

Supplementary Materials for

Reveal the Alignment of Defects in a Metal-Organic Framework with Tunable Flexibility

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Materials and Methods

Materials

The compound 4,4'-dihydroxy-(1,1'-biphenyl)-3,3'-dicarboxylic acid ($H_4dobpdc$) was obtained from Trylead Chemical Technology Co., Ltd. All other reagents and solvents were obtained from Sigma-Aldrich at reagent grade purity or higher and were used without further purification.

The defective $Mg_2(dobpdc)$ and ideal $Mg_2(dobpdc)$ were synthesized by the same method, albeit with different amounts of 4-fluorosalicic acid (see Table S1). The ligand $H_4dobpdc$ (0.411 g, 1.5 mmol), $Mg(NO_3)_2 \cdot 6H_2O$ (1.15 g, 4.5 mmol) and 4-fluorosalicic acid (quantities given in Table S1) were dissolved in 30 mL of a 55 : 45 (volume : volume) methanol: N,N-dimethylformamide (DMF) solution using sonication. Once all reagents were dissolved, the synthesis mixtures were transferred to a 50 mL Teflon liner. The liners were sealed in stainless-steel autoclaves which were subsequently placed in an oven preheated to 120 °C for 24 h. The crude white powder precipitates were isolated by filtration and were then soaked in 50 mL of DMF for 12 h at 120 °C for three times, followed by solvent exchange by soaking in 50 mL of methanol for 12 h at 60 °C for three times. The methanol-solvated frameworks were collected by filtration and labelled as “wet” samples. Then, the “wet” samples were dried under vacuum for a minimum of 3 h at room temperature to remove the free methanol and yielded “dry” samples. The “dry” powders were re-soaked with methanol solvent overnight and then collected by filtration to obtain the “rewet” samples.

Methods

To analyze the loading of Fs^{2-} ligand, ~5 mg of each defective $Mg_2(dobpdc)$ powder was digested in a solution of 0.4 mL of 35 wt. % DCl in D_2O and 1 mL of DMSO- d_6 containing a known-concentration of 1,3,5-trimethoxybenzene (as the internal standard for quantitation). The solution was sonicated and/or heated at 60 °C until the solid fully dissolved. 1H NMR spectra were acquired on Bruker AV-300, ABV-400, or AVQ-400 instruments at the University of California, Berkeley NMR facility. The actual Fs^{2-} and $dobpdc^{4-}$ concentrations in MOF samples were determined from the 1H signals of Fs^{2-} and $dobpdc^{4-}$ relative to that of the internal standard.

Powder X-ray diffraction (PXRD)_measurements were carried out on samples placed on a quartz holder using a Rigaku Ultimate-IV X-ray diffractometer operated at 40 kV/30 mA with Cu $K\alpha$ line ($\lambda = 1.5418 \text{ \AA}$). Patterns were collected in reflectance Bragg-Brentano geometry in the 2θ range from 3 to 50°.

The morphologies of MOF samples were observed on a field emission scanning electron microscope (HITACHI SU8000 FE-SEM) at 5 kV.

Nitrogen sorption measurements were performed at 77 K on BelSorp-max instrument. Prior to adsorption measurements, the $Mg_2(dobpdc)$ samples were pretreated (activated) under vacuum for 24 h at 250 °C. Brunauer-Emmett-Teller (BET) surface areas were calculated by fitting the isotherm data in the P/P_0 range of 0 to 0.1.

Thermogravimetric analyses (TGA) were conducted using a TA Instruments TGA Q5000 with a flow rate of 25 mL/min for N_2 gas. Thermogravimetric decomposition traces were collected under 100% N_2 with a temperature ramp rate of 1.5 °C/min (Figures S2).

Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was conducted on an ICP Optima 7000 DV instrument. ~ 10 mg of MOF were sonicated and fully digested in 0.4 mL of 35 wt. % HCl solution and 1 mL of DMSO. 50 μ L dissolved MOF

solutions were diluted with 10 mL pure H₂O. The diluted solutions were used to test the magnesium contents by ICP-OES. The Mg²⁺ concentration (mg/L) in different MOF samples was experimentally determined by referring to a magnesium standard curve made by Mg(NO₃)₂ solution.

Supplementary Text

Solid-state NMR Experiments

Solid-state NMR experiments were performed on a Bruker Avance 400 III HD spectrometer (magnetic field strength 9.4 T) operating at resonance frequencies of 400.13 MHz for ¹H, 376.8 MHz for ¹⁹F, and 100.61 MHz for ¹³C, using a HFX magic-angle spinning (MAS) probe equipped with a 3.2 mm spinner module. The spinning speed was 15 kHz for all the experiments. The ¹³C signals were referenced to the methylene signal of adamantane at 38.5 ppm, and ¹⁹F signals were referenced to that of ammonium trifluoroacetate at -72.0 ppm.

For the ¹³C cross polarization (CP) spectra, the ramped CP sequence was applied and the ¹³C signal was acquired under SPINAL-64¹ ¹H decoupling (100 kHz ¹H radiofrequency field). The contact times of 50 or 4000 μs was used for ¹H-¹³C polarization transfer. The recycle delays for ¹⁹F experiments were 10 s to ensure the full return of the ¹⁹F magnetization to equilibrium. Pulse lengths were 2.5 μs for ¹H 90° pulse, 2.4 μs for ¹⁹F 90° pulse, and 3.0 μs for ¹³C 90° pulse.

For ¹³C{¹⁹F} rotation echo dipolar recoupling (REDOR)² experiments, the standard pulse sequence with ¹³C detection and ¹⁹F recoupling pulses was used (drawn in Scheme S1). The REDOR experiments with (S) and without (S₀) 180° pulses on the ¹⁹F channel were acquired for different recoupling times. The ratio of signal intensities (S/S₀) for different recoupling times gives a REDOR curve.

The pulse sequence for ¹⁹F centerband-only detection of exchange (CODEX)³ experiment is shown in Scheme S2. Two experiments, an exchange experiment (S) with variable spin diffusion mixing time t_m and a short delay Δ (1 ms), and a reference experiment (S₀) with interchanged t_m and Δ, were acquired. The ratio of intensities, S/S₀, was measured as a function of the mixing time until it reached a plateau. Total suppression of spinning sidebands (TOSS) was used to eliminate spinning sidebands.

Computational Methods

(1) Structural motifs of defective Mg₂(dobpdc)

The structural motifs of defective Mg₂(dobpdc) are depicted by stacked hexagons (Scheme S3). A black edge represents a single dobpdc⁴⁻ linkers and a red edge represents two Fs²⁻ ligands. Hypothetical defect distributions in defective MOF 0.32D are shown in Scheme S3. The distribution motifs are named as XYZ_n or XY_n, where X, Y, or Z represent the number of red edges in each hexagonal layer and the subscript *n* represents different scenarios. For building a hybrid superlattice of 1D aligned defects, we combined 222₂, 222₃, and 222₄ motifs.

(2) Molecular dynamics simulations

Structures of ideal and defective Mg₂(dobpdc) with incorporated methanol were optimized by density function theory (DFT) calculations at the level of B3LYP functional. The basis set of 6-31G* was used for C, H, O and Mg atoms. These calculations were performed by Gaussian 09 package⁴. The parameters of methanol and the defective Mg₂(dobpdc) used in molecular dynamics (MD) simulations were obtained in General Amber Force Field form by Antechamber tool⁵. RESP method was applied to determine the charge of MOFs and methanol molecules⁶.

MD simulations were performed in the NPT ensemble in GROMACS package⁷⁻⁹ (version 5.0.4). For the “wet” condition, the MOF matrices were fulfilled with methanol through PACKMOL package¹⁰. For the “dry” condition, the free methanol molecules were removed and the coordinated methanol molecules were retained. Each simulation was performed for 50 nanoseconds with a time step of 2 fs. Data is saved every 4 ps. Periodic boundary conditions were applied in all simulations. Nose-Hoover thermostat coupling method was used to maintain the temperature at 300 K¹¹. The bond length was constrained by linear constraint solver algorithm in the simulations¹². For non-bonded van der Waals interaction, the cut-off switching function started at 1.2 nm and reached zero at 1.35 nm. For long-range electrostatic interaction calculated by particle mesh Ewald summation method¹³, the cut-off distance was set at 1.2 nm. The distance distribution analysis of ¹³C-¹⁹F atoms and REDOR calculations¹⁴ were obtained from the last 1 ns of MD simulation. The VMD software was used to visualize simulation results¹⁵.

(3) DFT energy calculations

Energy difference, $\Delta\Delta E$, between defective $\text{Mg}_2(\text{dobpdc})$ and ideal $\text{Mg}_2(\text{dobpdc})$ was calculated by the formula below:

$$\Delta\Delta E = (E_{\text{total, defect}} - E_{\text{total, ideal}}) - (E_{\text{Fs}^{2-}} - E_{\text{dobpdc}^{4-}})$$

Here, $E_{\text{total, defect}}$ is the absolute energy of the defective MOF; $E_{\text{total, ideal}}$ is the absolute energy of the ideal MOFs; $E_{\text{Fs}^{2-}}$ is the absolute energy for the Fs^{2-} ligands in defective MOFs; and $E_{\text{dobpdc}^{4-}}$ is the absolute energy of the dobpdc^{4-} linkers in ideal MOFs. The absolute energy is calculated by DFT calculations at the level of B3LYP functional with basis 6-31G basis set in Gaussian 09 package.

Powder XRD Analysis

Pawley refinement of the powder diffraction data was carried using TOPAS-ACADEMIC 4.1^{16,17}. We first refined the data for the ideal “wet” sample, allowing the lattice parameters and peak shape to vary freely. For all other samples, the lattice parameters were freely refined but the peak shape was modelled using the peak shape of the ideal “wet” sample plus an additional Gaussian size broadening term. From this Gaussian size broadening an effective crystallite size was determined. For all structures the space group of ideal material was used (P3121).

The first two Bragg peaks, {100} and {110}, were modelled using a pseudo-Voigt peak shape, where peak position, area and Lorentzian contribution were allowed to vary freely for each peak. The background was fitted using two term Chebyshev polynomial (i.e. a linear and constant term). An additional exponential convolution was applied (Simple Axial model) to account for instrumental peak asymmetry. From these refinements we determined the relative peak intensities of the first two Bragg peaks.

Table S1. Quantities of 4-fluorosalicylic acid used in the synthesis of ideal and defective Mg₂(dobpdc) samples.

Sample	Amount of 4-fluorosalicylic acid used in synthesis
Ideal	0
0.03D	23.4 mg (0.15 mmol)
0.09D	70.2 mg (0.45 mmol)
0.19D	163.9 mg (1.05 mmol)
0.26D	351.2 mg (2.25 mmol)
0.32D	585.4 mg (3.75 mmol)

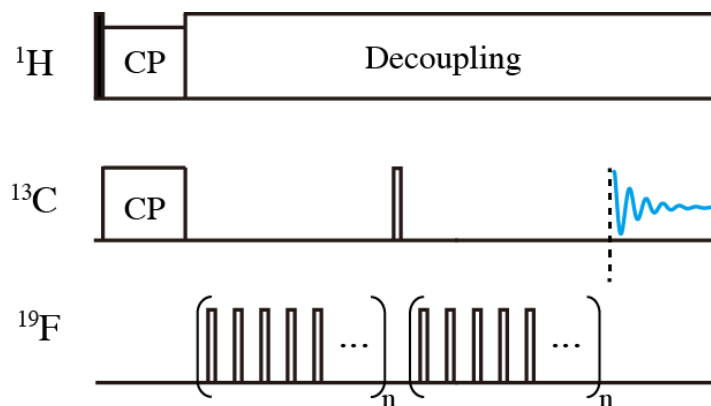
Table S2. Quantitative data extracted from the solution-state ¹H NMR.

Sample	Fs ²⁻ to dobpdc ⁴⁻ molar ratios ($\frac{n(\text{Fs}^{2-})}{n(\text{dobpdc}^{4-})}$)
Ideal	0
0.03D	0.06
0.09D	0.20
0.19D	0.46
0.26D	0.72
0.32D	0.95

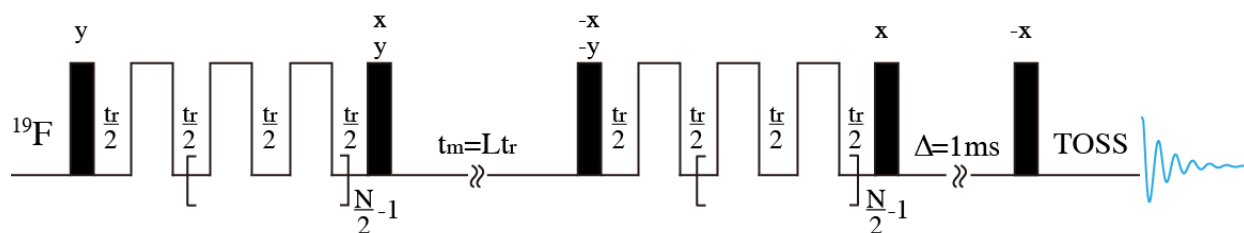
Table S3. The concentrations of different components in Mg₂(dobpdc). The concentration of dobpdc⁴⁻ linker C(dobpdc⁴⁻) and the concentration of Fs²⁻ ligand C(Fs²⁻) were obtained from solution-state ¹H NMR. The concentration of Mg²⁺ C(Mg²⁺) was determined by ICP-OES.

Unit: mmol/g

Sample	C(dobpdc ⁴⁻)	C(Fs ²⁻)	C(Mg ²⁺)	$\frac{C(\text{dobpdc}^{4-})}{C(\text{Mg}^{2+})}$	$\frac{C(\text{Fs}^{2-})}{C(\text{Mg}^{2+})}$	$\frac{2 \times C(\text{dobpdc}^{4-}) + C(\text{Fs}^{2-})}{C(\text{Mg}^{2+})}$
Ideal	2.30	0.00	4.46	0.52	0.00	1.03
0.03D	2.25	0.13	4.50	0.50	0.03	1.03
0.09D	2.01	0.40	4.50	0.45	0.09	0.98
0.19D	1.81	0.83	4.60	0.39	0.18	0.97
0.26D	1.67	1.20	4.46	0.38	0.27	1.02
0.32D	1.55	1.47	4.41	0.35	0.33	1.04

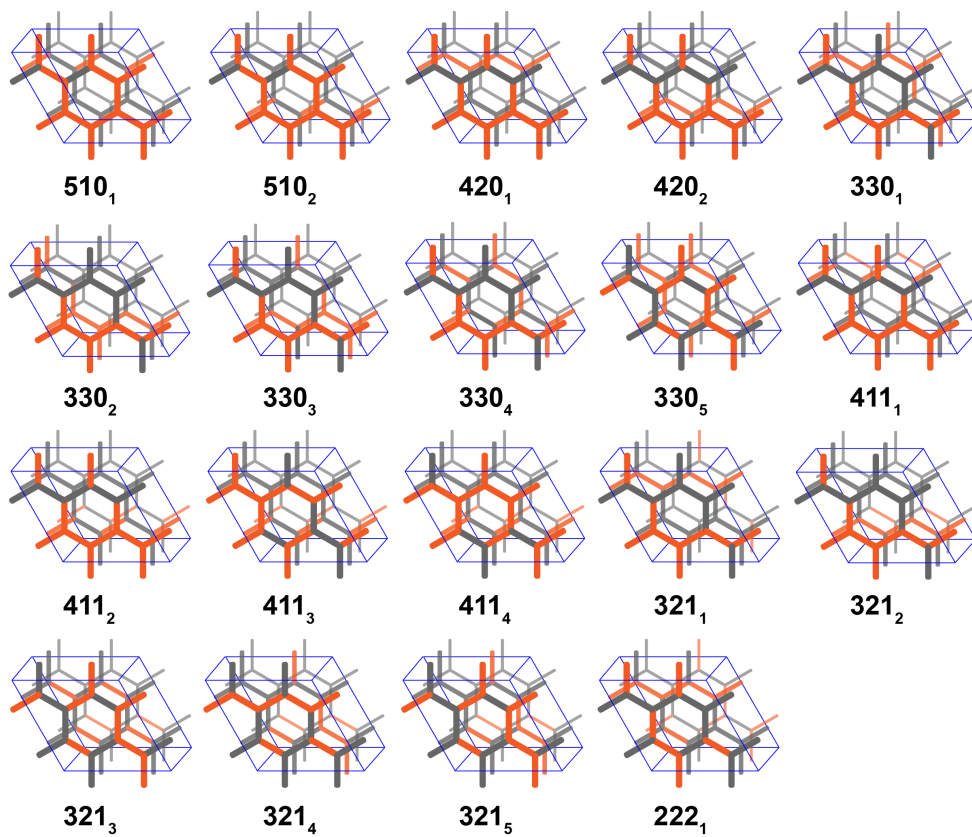


Scheme S1. $^{13}\text{C}\{^{19}\text{F}\}$ REDOR pulse sequence with ^{19}F 180° recoupling pulses.

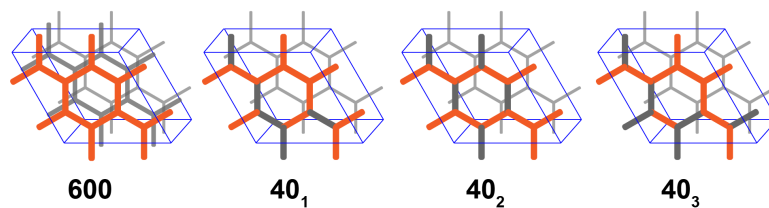


Scheme S2. ^{19}F CODEX pulse sequence. 90° pulses are shown as black, 180° pulses as white.

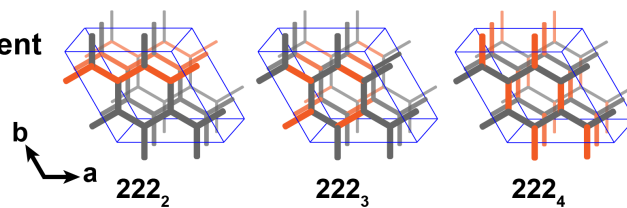
3D Random



2D Planar



1D Alignment



Scheme S3. Hypothetical motifs for defect distribution in defective Mg₂(dobpdc).

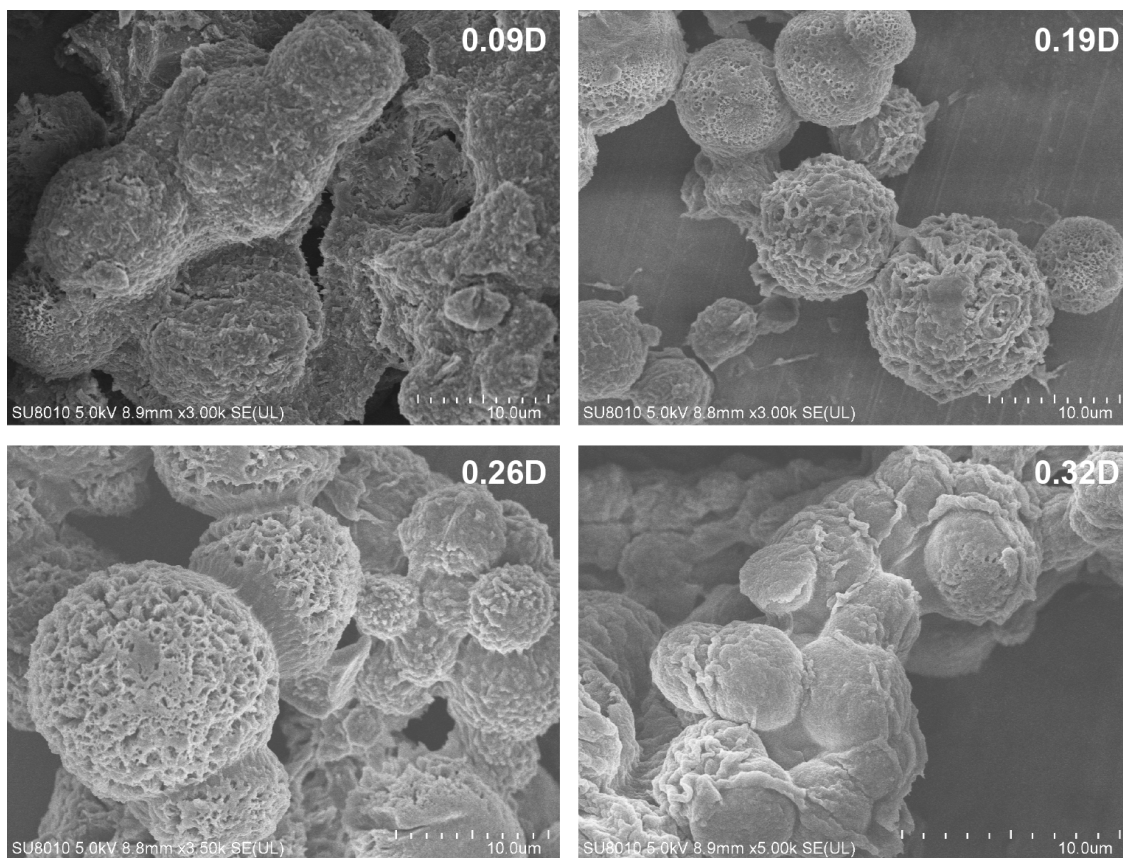


Figure S1. SEM images of defective $\text{Mg}_2(\text{dobpdc})$ samples. Scale bar: 10 μm .

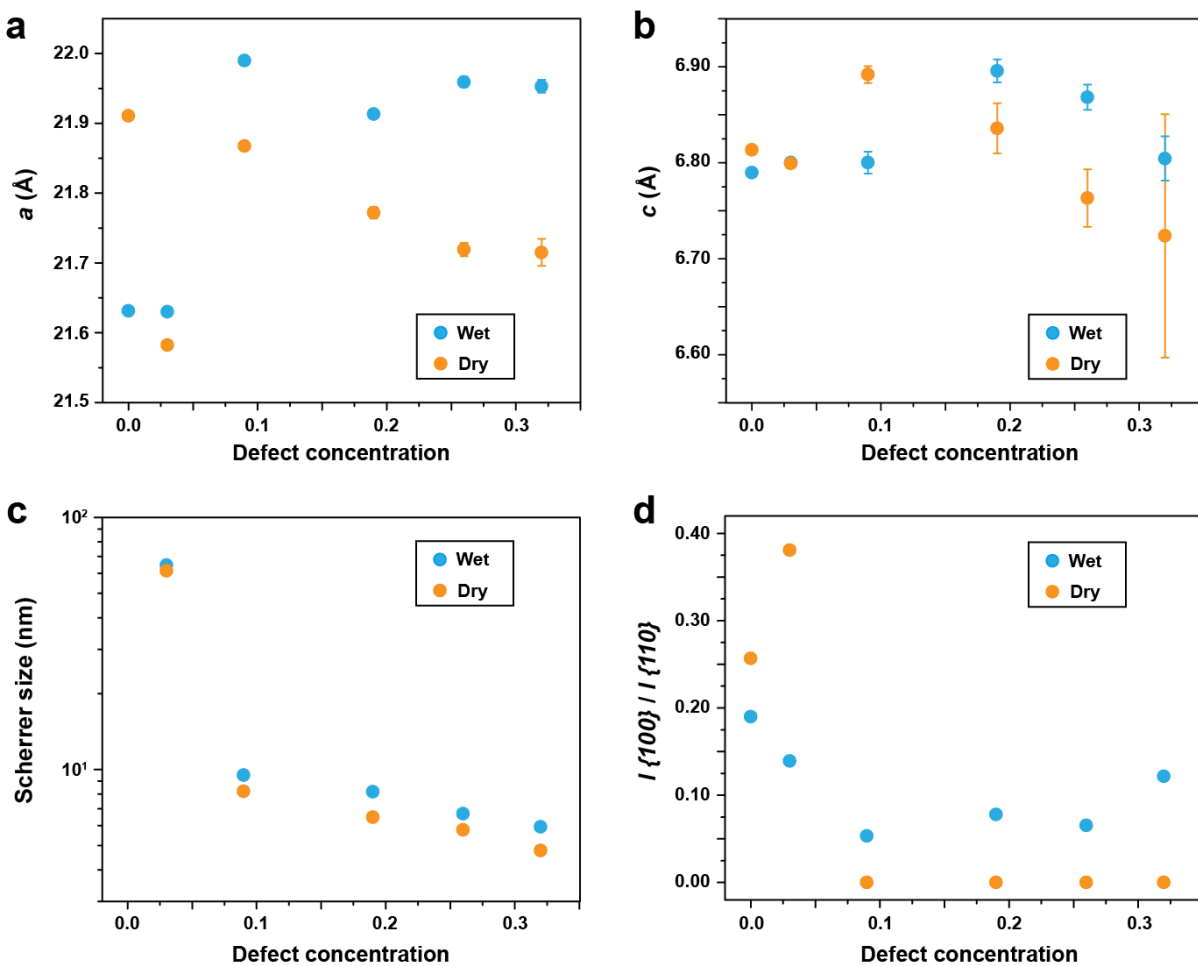


Figure S2. The results of the Pawley refinement of PXRD patterns of $\text{Mg}_2(\text{dobpdc})$ with various defect concentrations. (a) Lattice parameter a ; (b) Lattice parameter c ; (c) Crystallite sizes estimated by Scherrer equation; (d) The intensity ratio of $\{100\}$ peak versus $\{110\}$ peak. The blue dots are for the “wet” samples and the orange dots are for the “dry” samples.

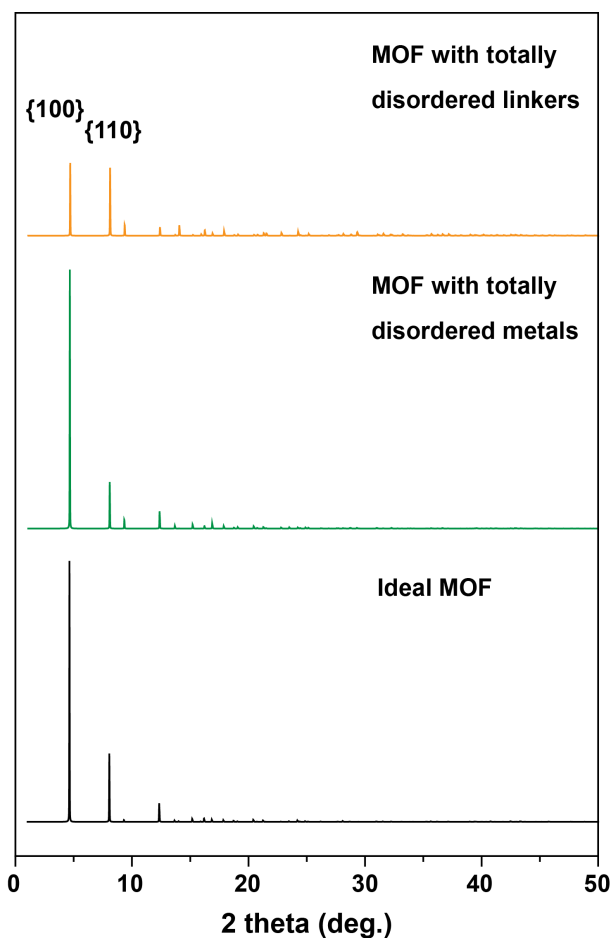


Figure S3. Simulated PXRD patterns of ideal $\text{Mg}_2(\text{dobpdc})$ and hypothetical $\text{Mg}_2(\text{dobpdc})$ structures. In the hypothetical models, the site occupancy of dobpdc^{4-} is deleted to represent the structure with disordered linkers; whereas the site occupancy of Mg^{2+} is deleted to represent the structure with disordered metals. Only for the hypothetical structure with disordered linkers, the relative intensity of $\{100\}$ is significantly reduced with respect to the $\{110\}$ peak. This feature is similar to the experimental results observed in Figure 1c. We therefore expect the disorder induced by Fs^{2-} ligands is largely responsible for the reduction of $\{100\}$ peak in the experimental PXRD patterns of defective $\text{Mg}_2(\text{dobpdc})$.

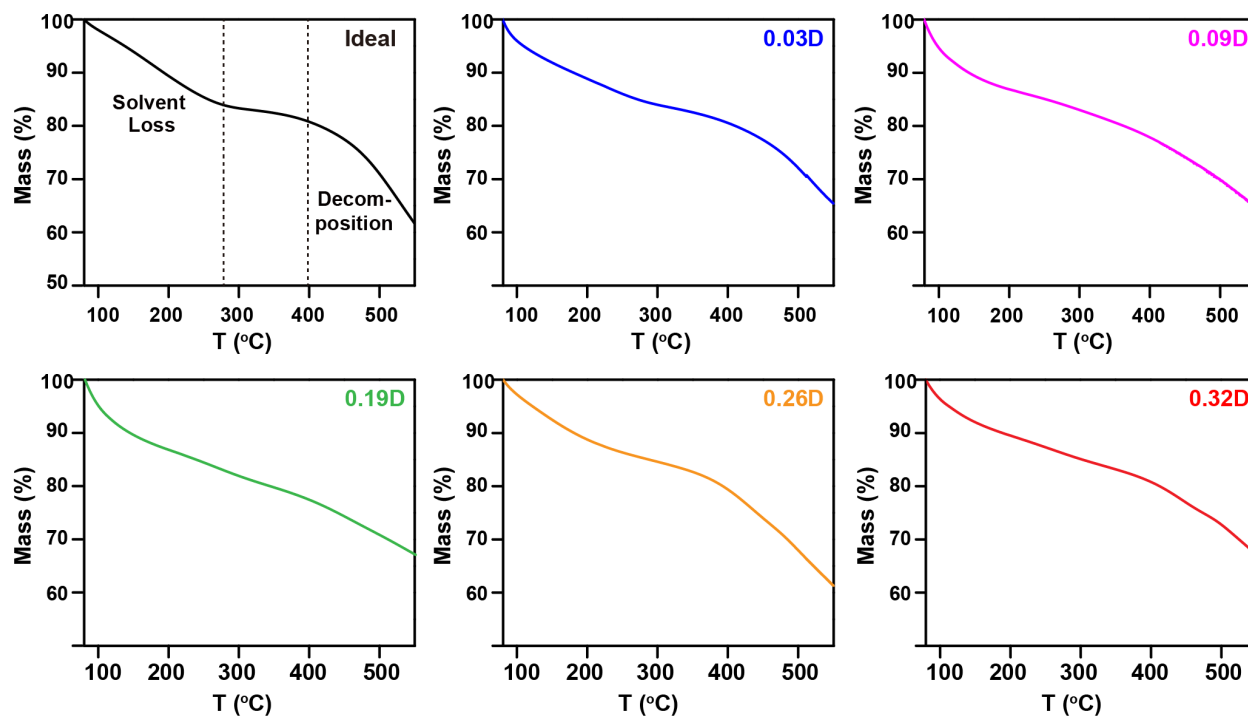


Figure S4. The results of thermogravimetric analysis under the flow of nitrogen. Temperature ramp rate was 1.5 °C/min. Both ideal and defective $\text{Mg}_2(\text{dobpdc})$ can withstand temperatures up to 400 °C without decomposition.

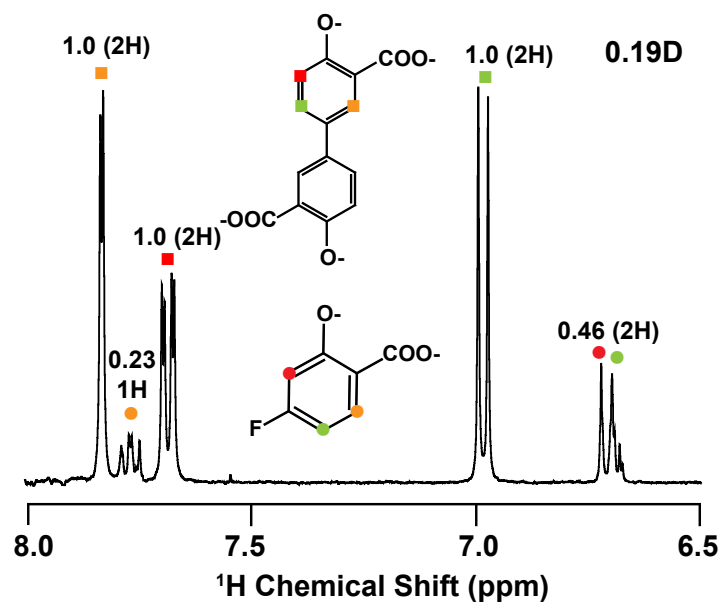


Figure S5. Solution-state ^1H NMR obtained on a defective $\text{Mg}_2(\text{dobpdc})$ sample (0.19D) digested in DCl solution. The integral areas are shown on the top of each ^1H peak.

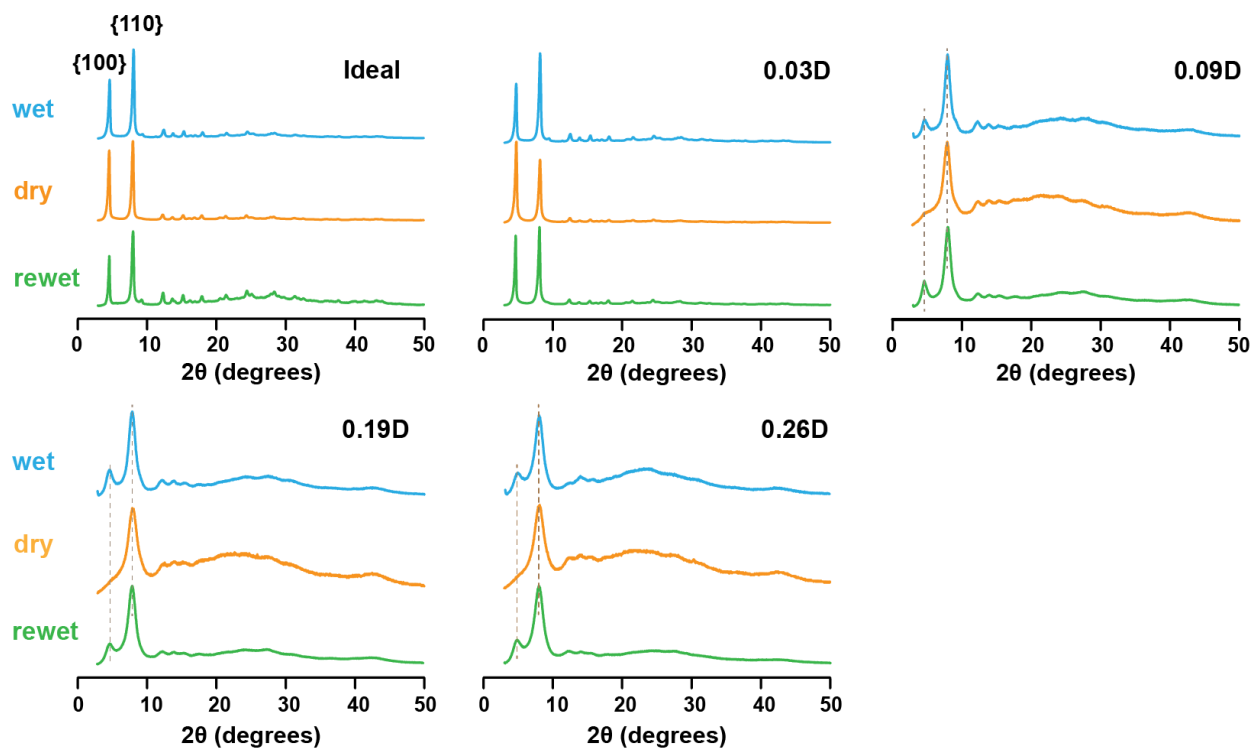


Figure S6. PXRD patterns of $\text{Mg}_2(\text{dobpdc})$ samples with various defect concentrations and under different post-synthetic treatment procedures. The “wet” samples are as-prepared samples with remaining methanol, the “dry” samples are the ones dried at room temperature under vacuum, and the “rewet” samples were obtained from the “dry” samples by re-soaking them with methanol.

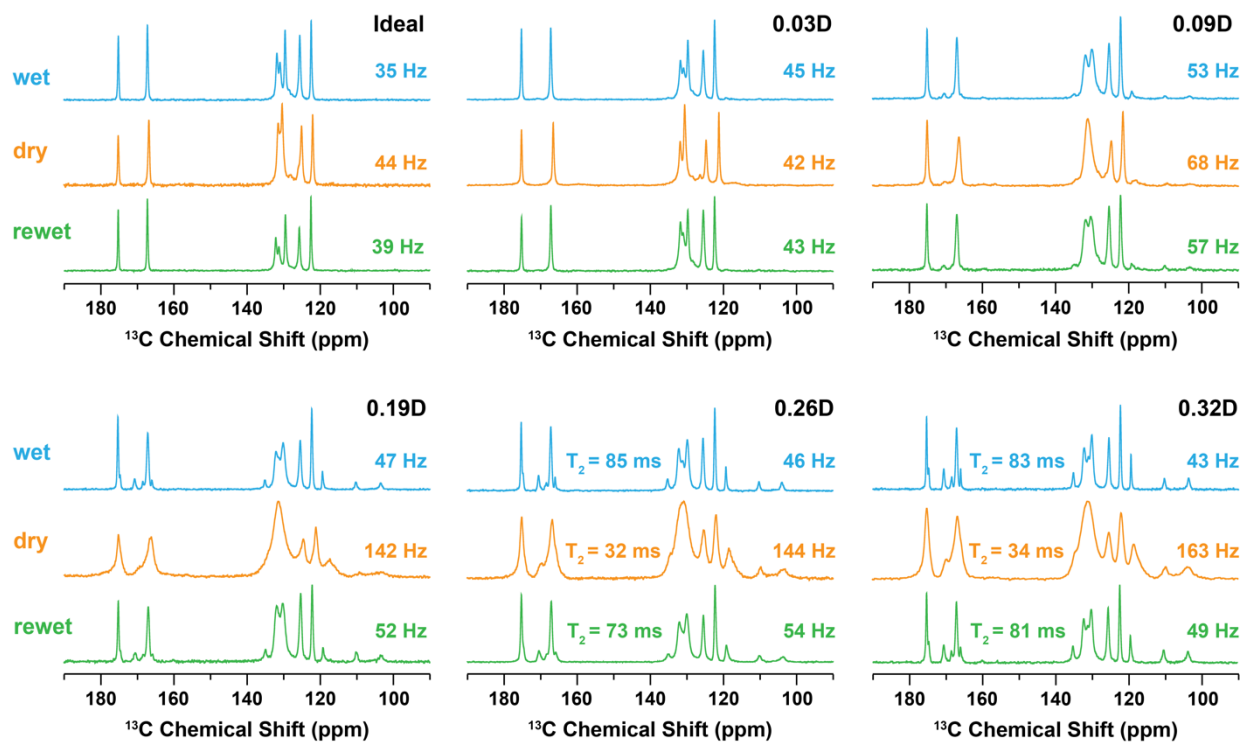


Figure S7. Comparison of ^{13}C CP NMR spectra obtained on $\text{Mg}_2(\text{dobpdc})$ samples under different conditions: “wet” (blue lines), “dry” (orange lines) and “rewet” (green lines). The FWHM of the peak at 122 ppm are indicated. The contributions to FWHM can be divided into two parts: the heterogeneous part that is due to local chemical bond disorder and the homogeneous part that is due to T_2 relaxation¹⁸: $\text{FWHM} = W_{\text{hetero.}} + W_{\text{homo.}}$, where $W_{\text{homo.}} = \frac{1}{\pi T_2}$. Since the $W_{\text{homo.}} < 10$ Hz in these samples, the major contribution in FWHM is $W_{\text{hetero.}}$.

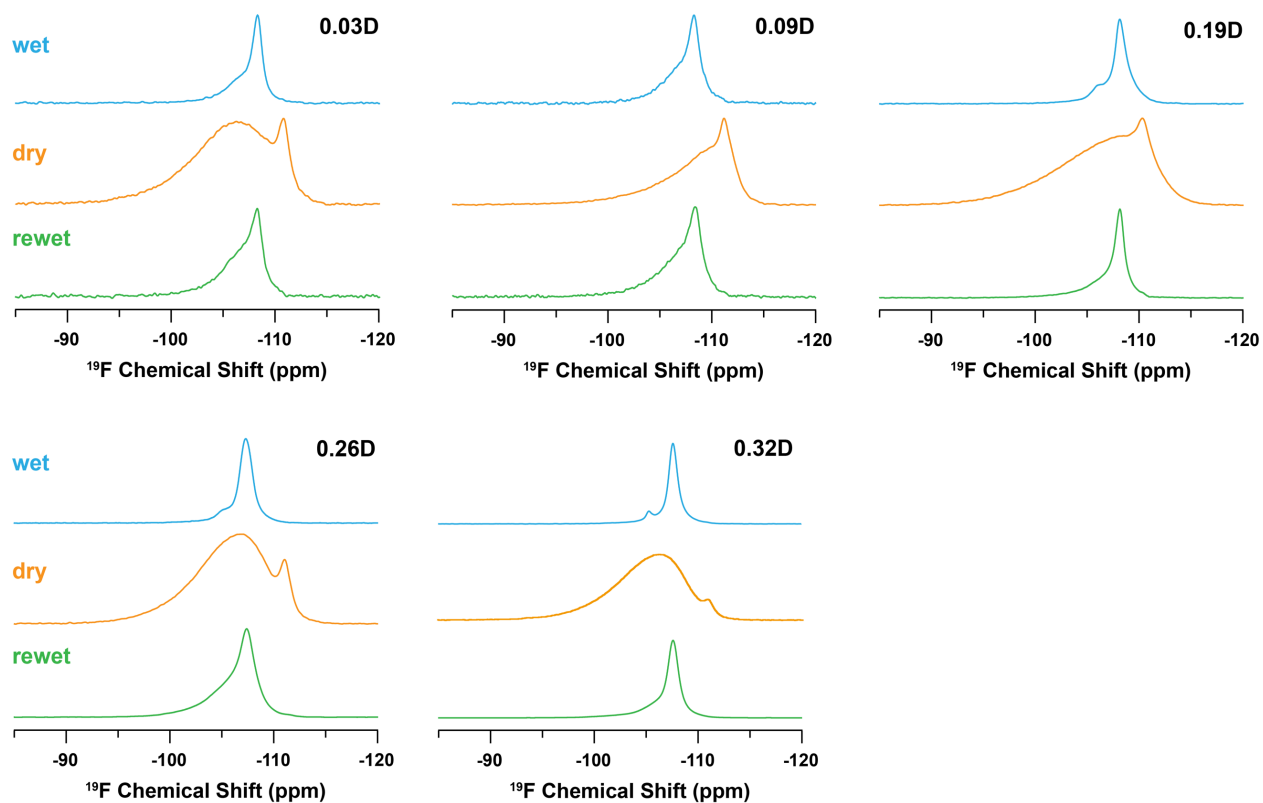


Figure S8. Comparison of ^{19}F NMR spectra obtained on the defective $\text{Mg}_2(\text{dobpdc})$ samples under different conditions: “wet” (blue lines), “dry” (orange lines) and “rewet” (green lines).

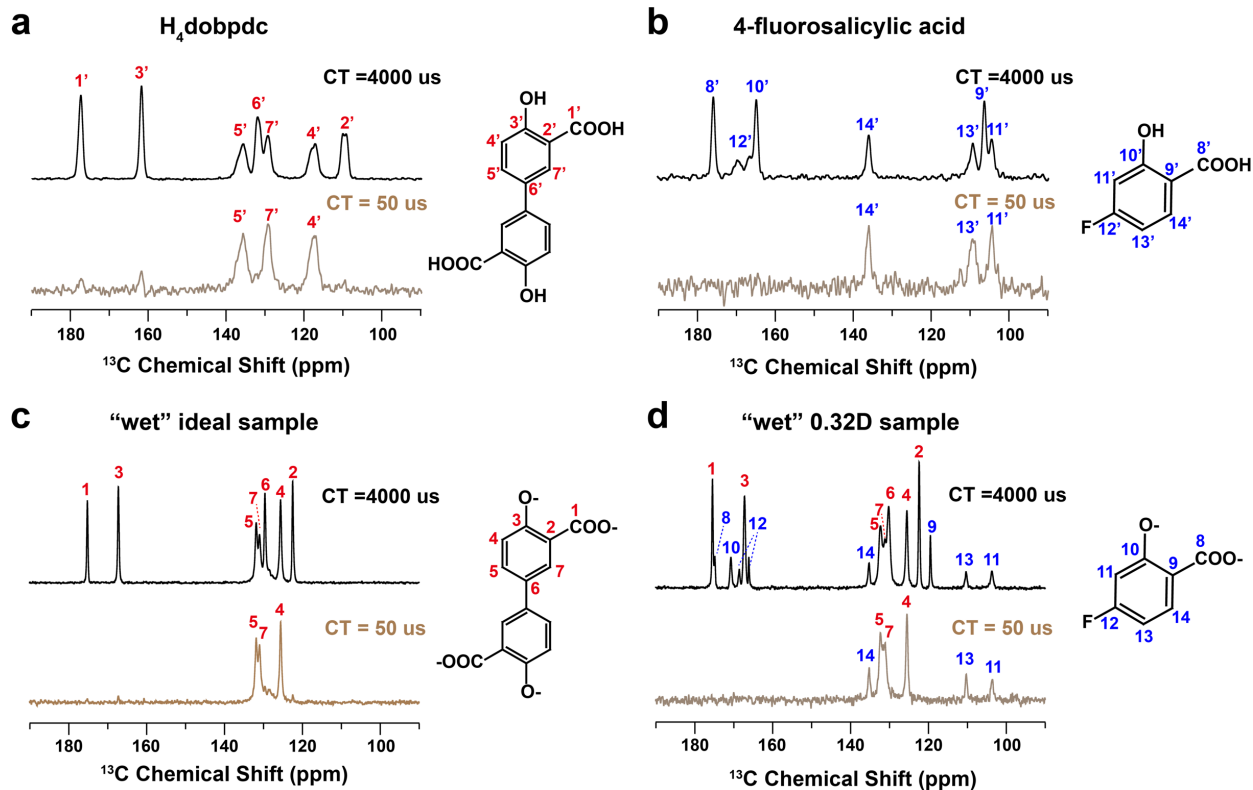


Figure S9. ^{13}C CPMAS spectra with a short contact time (CT=50 us, showing the carbons directly bonded by H) and with a long contact time (CT=4000 us, showing all carbon sites) for samples: (a) $H_4dobpdc$; (b) 4-fluorosalicilic acid; (c) “Wet” ideal sample; (d) “Wet” 0.32D sample. In addition, ChemDraw NMR predictor software was used to assist the assignment of ^{13}C peaks.

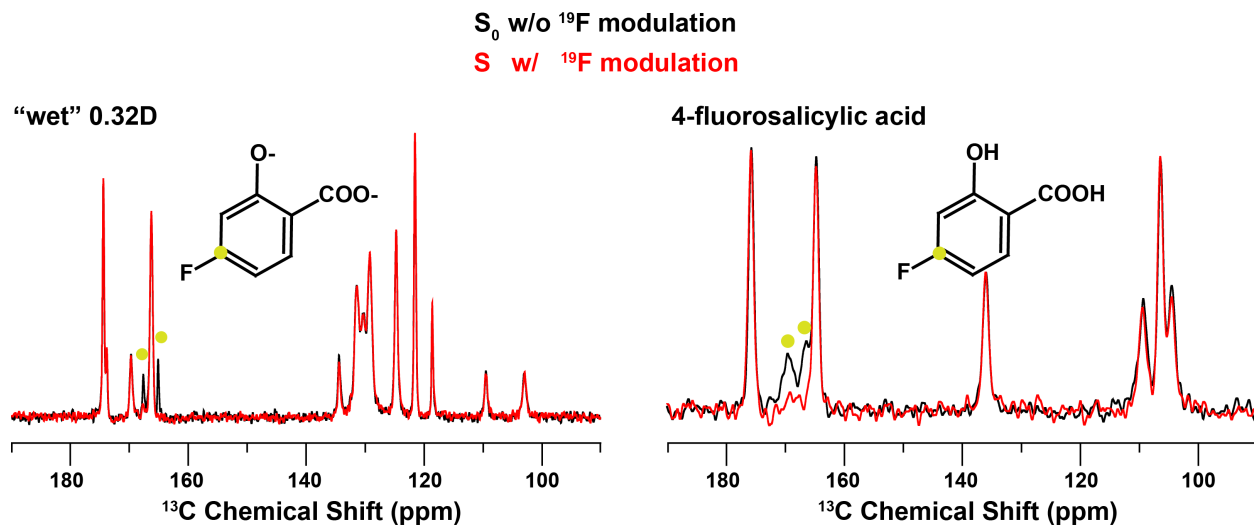


Figure S10. A suite of ^{13}C spectra obtained from a $^{13}\text{C}\{^{19}\text{F}\}$ REDOR experiment with a recoupling time of 67 μs on (left) the “wet” 0.32D sample and (right) 4-fluorosalicic acid. Black, the ^{13}C spectrum taken without ^{19}F irradiation (S_0); red, the ^{13}C spectrum with ^{19}F irradiations (S). The fast decaying peaks are attributed to the carbon that directly bonds to the fluorine on Fs^{2-} ligand or 4-fluorosalicic acid (yellow dots).

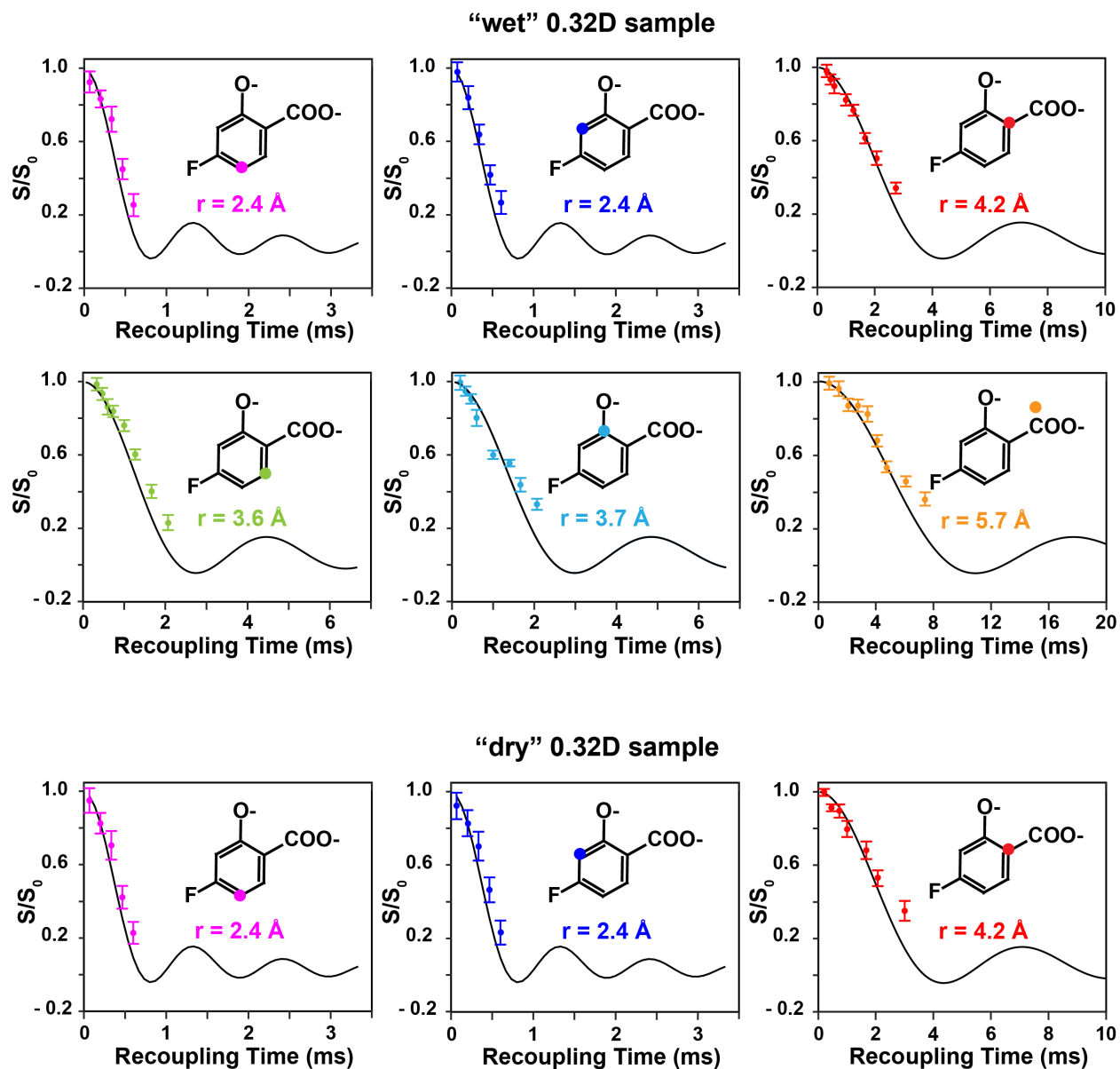


Figure S11. Experimental data points of $^{13}\text{C}\{^{19}\text{F}\}$ REDOR for corresponding carbon sites on the Fs^{2-} ligand. The black curves are theoretical REDOR decays for isolated ^{13}C - ^{19}F spin pairs of corresponding distance r . The well match between experimental data and calculated REDOR curves indicates that the Fs^{2-} ligand is rigid in both the wet and the dry samples.

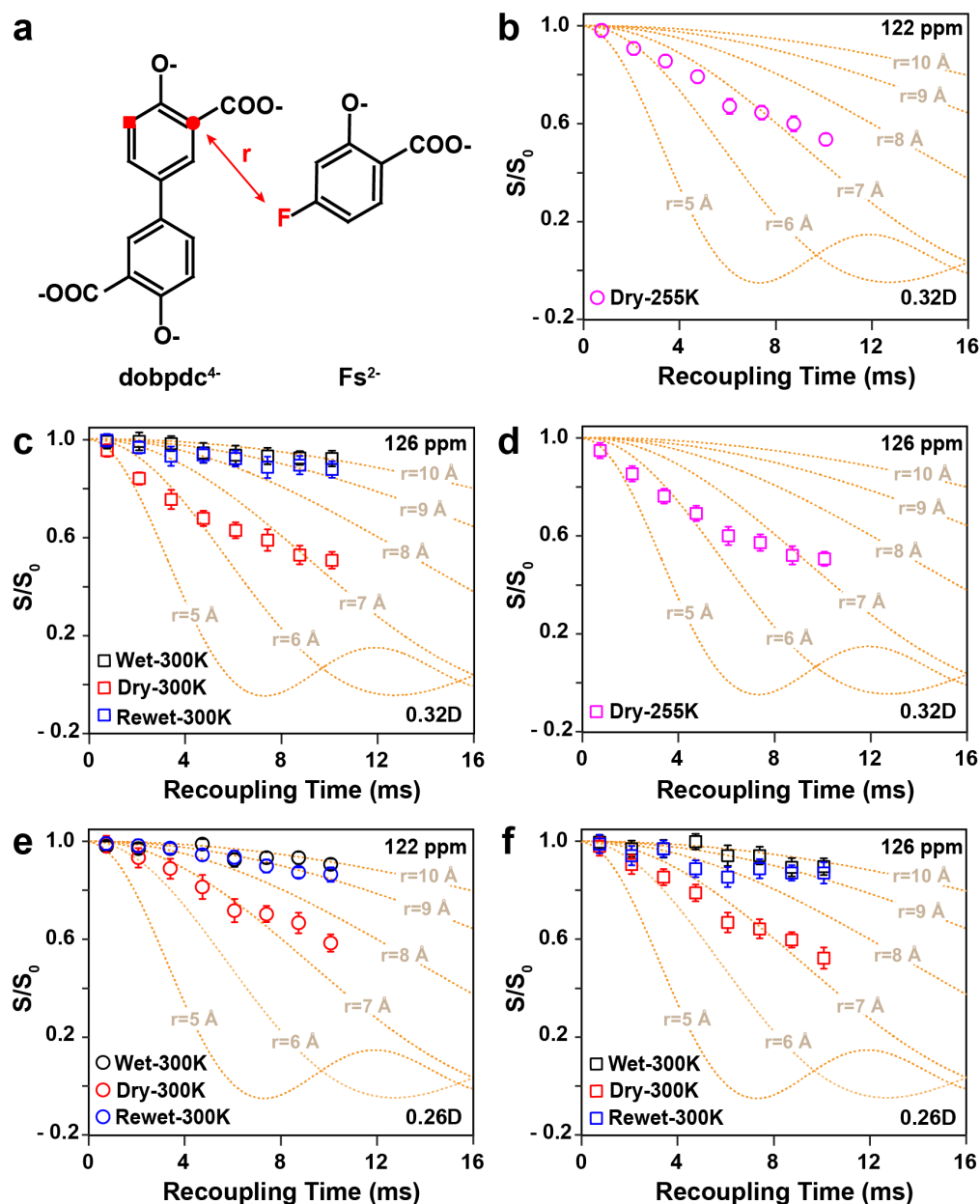


Figure S12. (a) Schematic illustration of the internuclear distance between the ^{13}C spins on the dobpcd^{4-} linker and the ^{19}F spin on the Fs^{2-} ligand. The red circles and squares are the corresponding peaks at 122 ppm and at 126 ppm, respectively. $^{13}\text{C}\{^{19}\text{F}\}$ REDOR curves for (b) the 122 ppm peak of the “dry” 0.32D sample measured at 255 K; (c) the 126 ppm peak of the 0.32D sample under different conditions measured at 300 K; (d) the 126 ppm peak of the “dry” 0.32D sample measured at 255 K; (e) the 122 ppm peak of the 0.26D sample under different conditions measured at 300K; (f) the 126 ppm peak of the 0.26D sample under different conditions measured at 300K. The dotted lines are spin dynamics simulations based on isolated ^{13}C - ^{19}F spin pairs of various internuclear distances. The results obtained at 255 K are identical with those obtained at 300 K again indicating the absence of motional effect. The differences between “wet” and “dry” samples can be observed on the REDOR decays of both 122 and 126 ppm peaks.

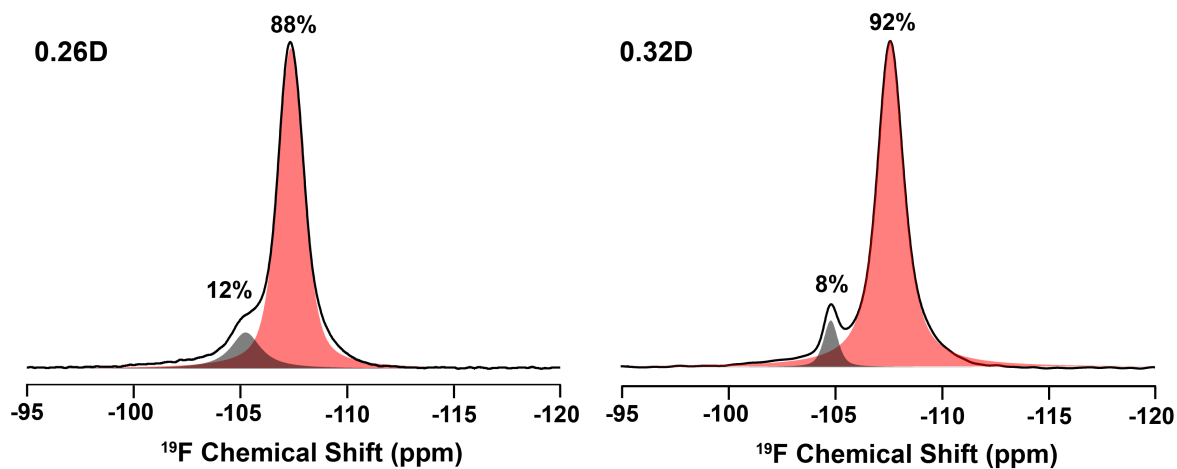


Figure S13. Quantitative direct excited ^{19}F NMR of the “wet” 0.26D and the “wet” 0.32D samples. The recycle delays were set to be 10 s. The percentages are the relative areas of the -108 ppm and the -105 ppm peaks.

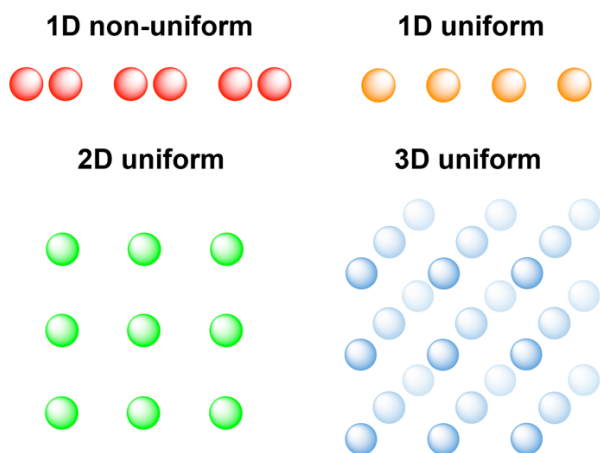


Figure S14. The schematic illustrations of hypothetical spatial distributions of ^{19}F spins in defective $\text{Mg}_2(\text{dobpdc})$.

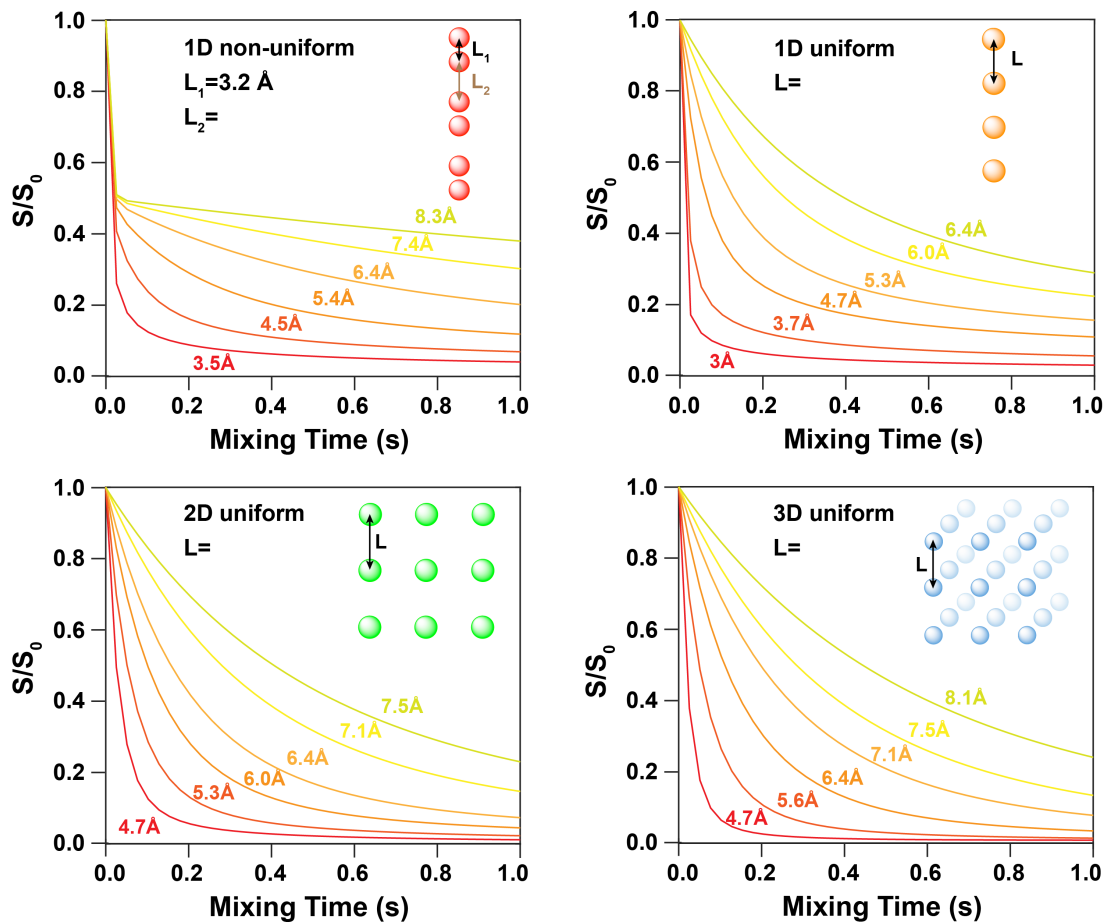


Figure S15. Numerical modeling of the CODEX decay curves for variable ^{19}F - ^{19}F separations based on different spatial geometries. Among the four models, only the 1D non-uniform distribution can give a strong biexponential decay that is consistent with experimental data. The distances shown in the plots were calculated based on an arbitrary constant proton spin diffusion rate.

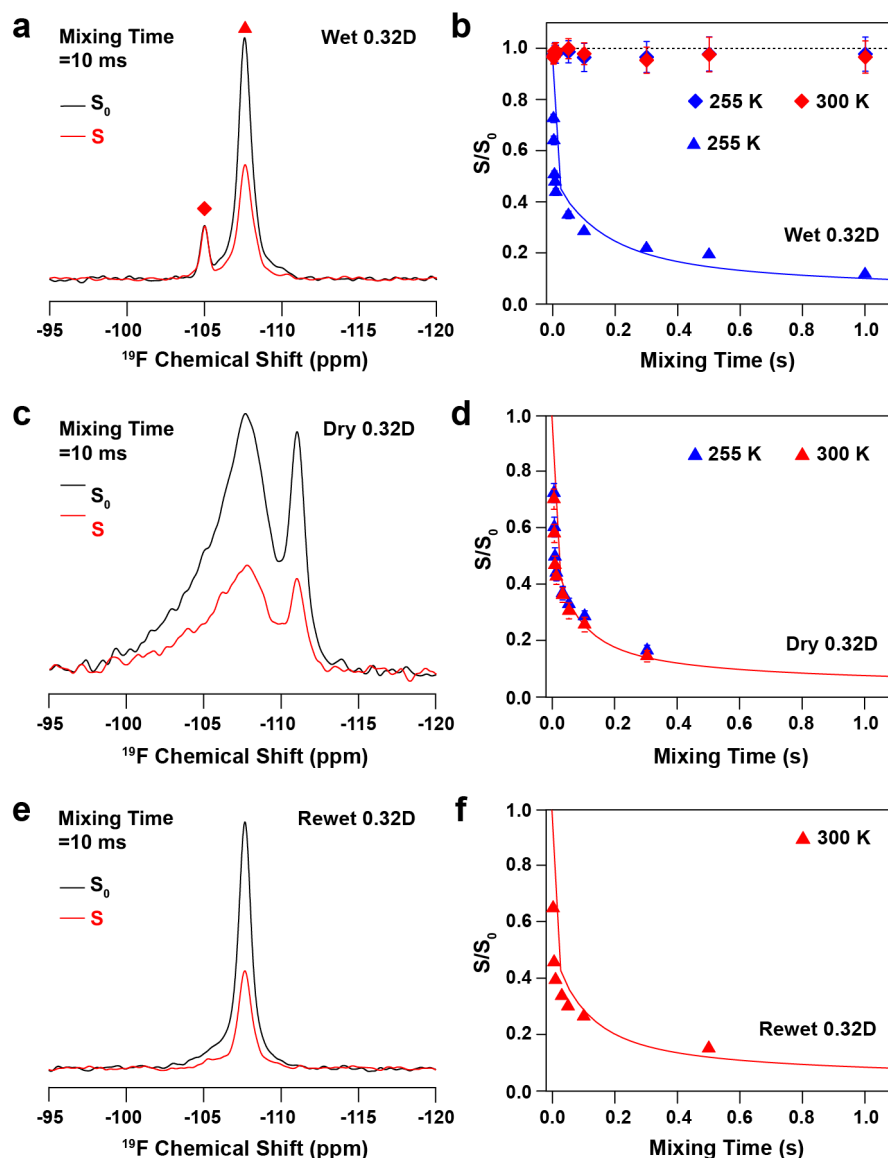


Figure S16. ^{19}F CODEX measurements for the 0.32D sample. (a) Representative ^{19}F CODEX spectra of the “wet” sample. The spectrum in red is the decay signal (S) and the spectrum in black is a reference experimental spectrum (S_0). (b) S/S_0 decay curves of the -108 ppm peak of the “wet” sample measured at 255 K (blue triangles) and of the -105 ppm peak measured at 255 K (blue diamonds) and at 300 K (red diamonds). (c) Representative ^{19}F CODEX spectra for the “dry” sample. (d) S/S_0 decay curves of the broad peak of the “dry” sample measured at 255 K (blue triangles) and 300 K (red triangles). (e) Representative ^{19}F CODEX spectra for the “rewet” sample. (f) S/S_0 decay curve of the -108 ppm peak of the “rewet” sample measured at 300 K (red triangles). The solid lines are the simulations based on 1D non-uniform distribution of ^{19}F spins. The almost identical decays obtained at 255 K and 300 K indicating the motional effect is neglectable.

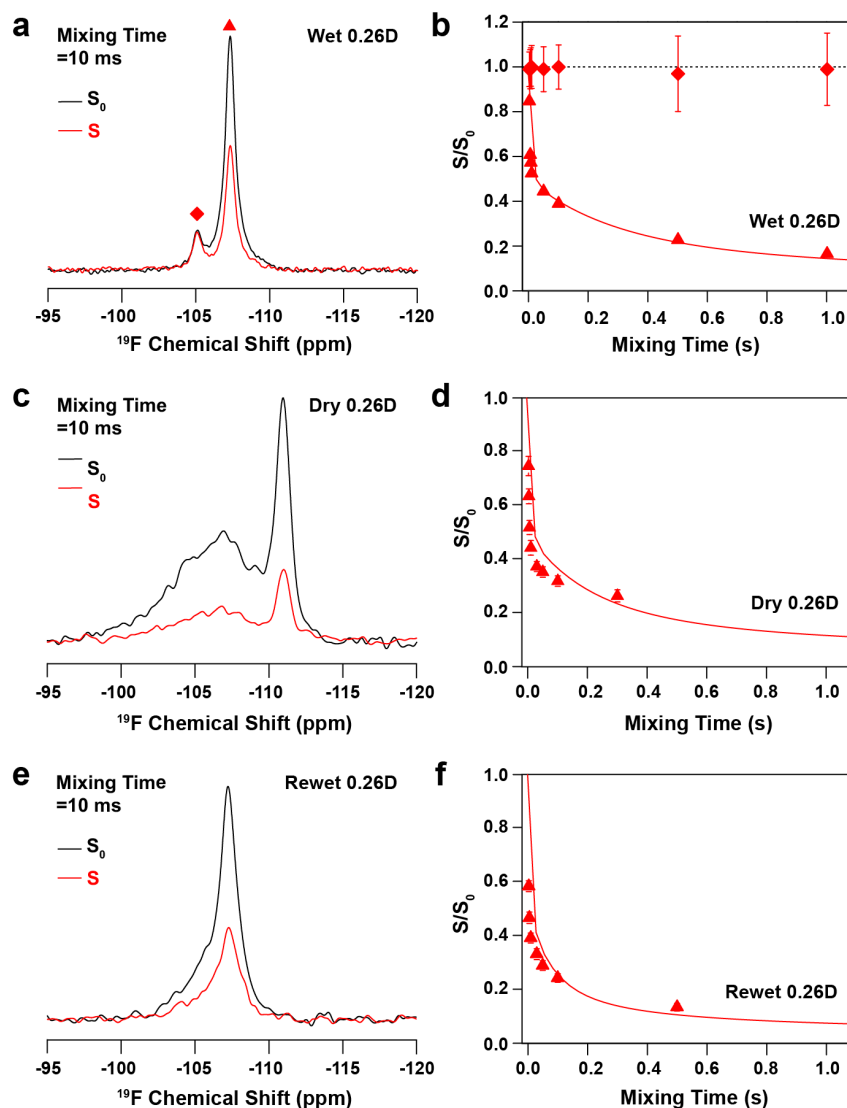


Figure S17. ^{19}F CODEX measurements for the 0.26D sample. (a) Representative ^{19}F CODEX spectra for the “wet” sample. The spectrum in red is the decay signal (S) and the spectrum in black is a reference experimental spectrum (S_0). (b) S/S_0 decay curves of the -108 ppm peak (triangles) and the -105 ppm peak (diamonds) of the “wet” sample measured at 300 K. (c) Representative ^{19}F CODEX spectra for the “dry” sample. (d) S/S_0 decay curve of the broad peak of the “dry” sample measured at 300 K (triangles). (e) Representative ^{19}F CODEX spectra for the “rewet” sample. (f) S/S_0 decay curve of the -108 ppm peak of the “rewet” sample measured at 300 K (triangles). The solid lines are the simulations based on 1D non-uniform distribution of ^{19}F spins.

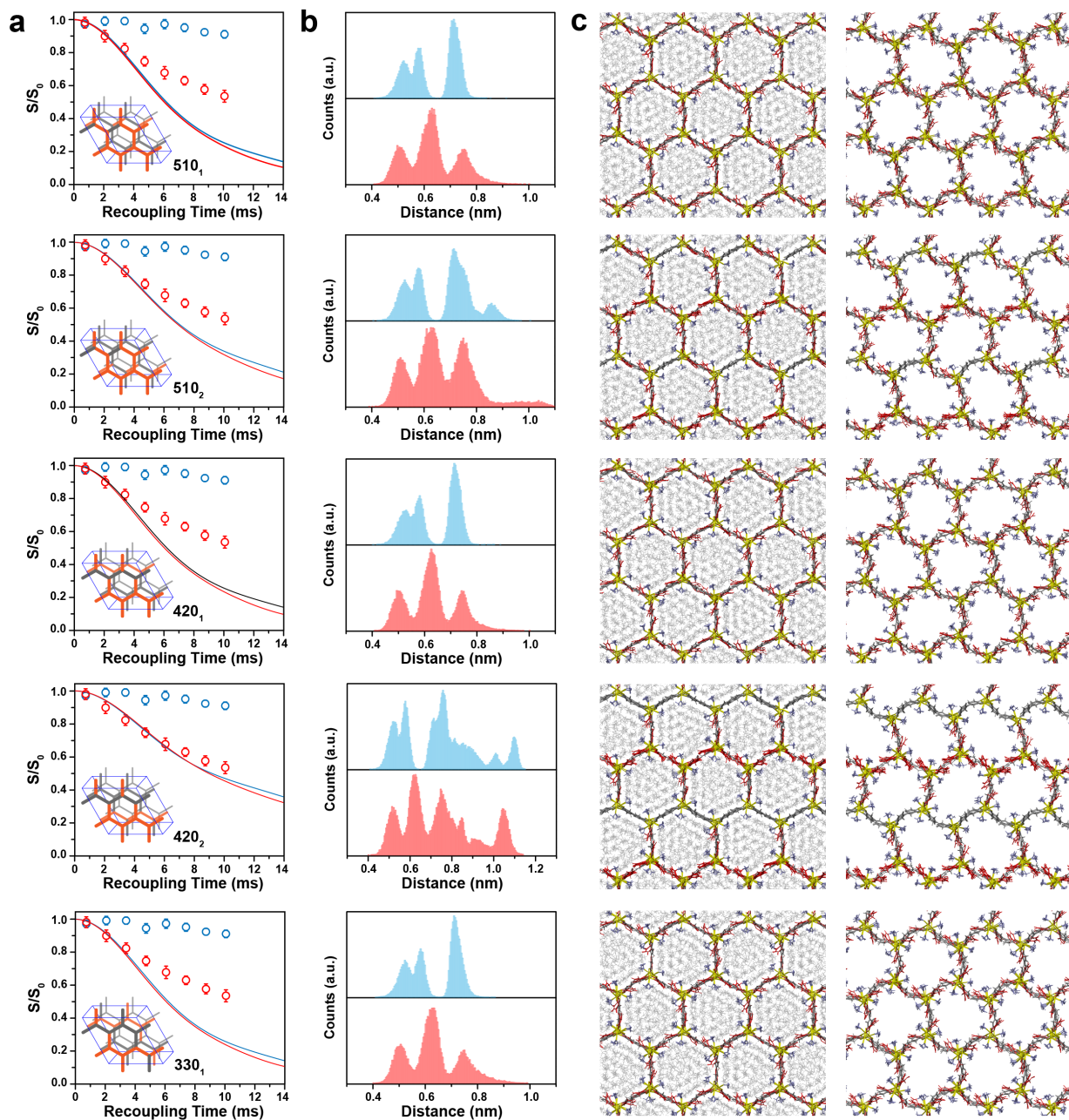


Figure S18. $^{13}\text{C}\{^{19}\text{F}\}$ REDOR investigations for hypothetical **3D random distributions** of defects in $\text{Mg}_2(\text{dobpdc})$. (a) The simulated REDOR curves for corresponding defect distribution motifs. The blue REDOR curves are for the “wet” sample and the red curves are for the “dry” sample according to the statistical ^{13}C - ^{19}F distances. Experimental REDOR data points are shown as open circles. (b) The simulated distribution of distances between the carbon at 122 ppm (on the dobpdc^{4-} linker) and their nearest F atoms (on the Fs^{2-} ligand) for “wet” (blue) and “dry” (red) conditions. (c) The snapshots of MD optimized superlattices for the “wet” or “dry” samples. Different colored sticks represent different components: red for Fs^{2-} ligands, grey for dobpdc^{4-} linkers, yellow for metal-oxygen atoms, light blue for coordinated methanol and silver for physically adsorbed methanol.

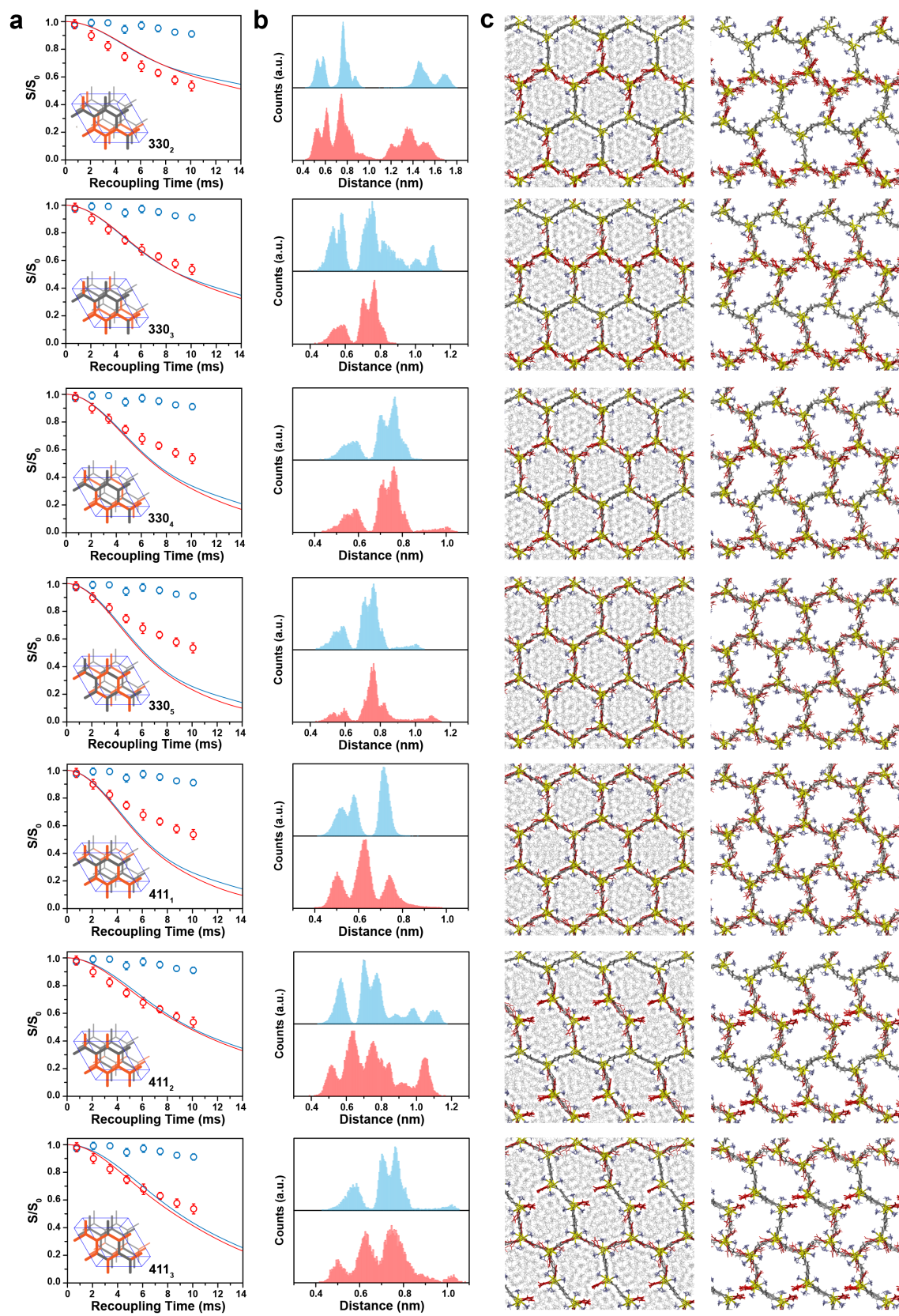
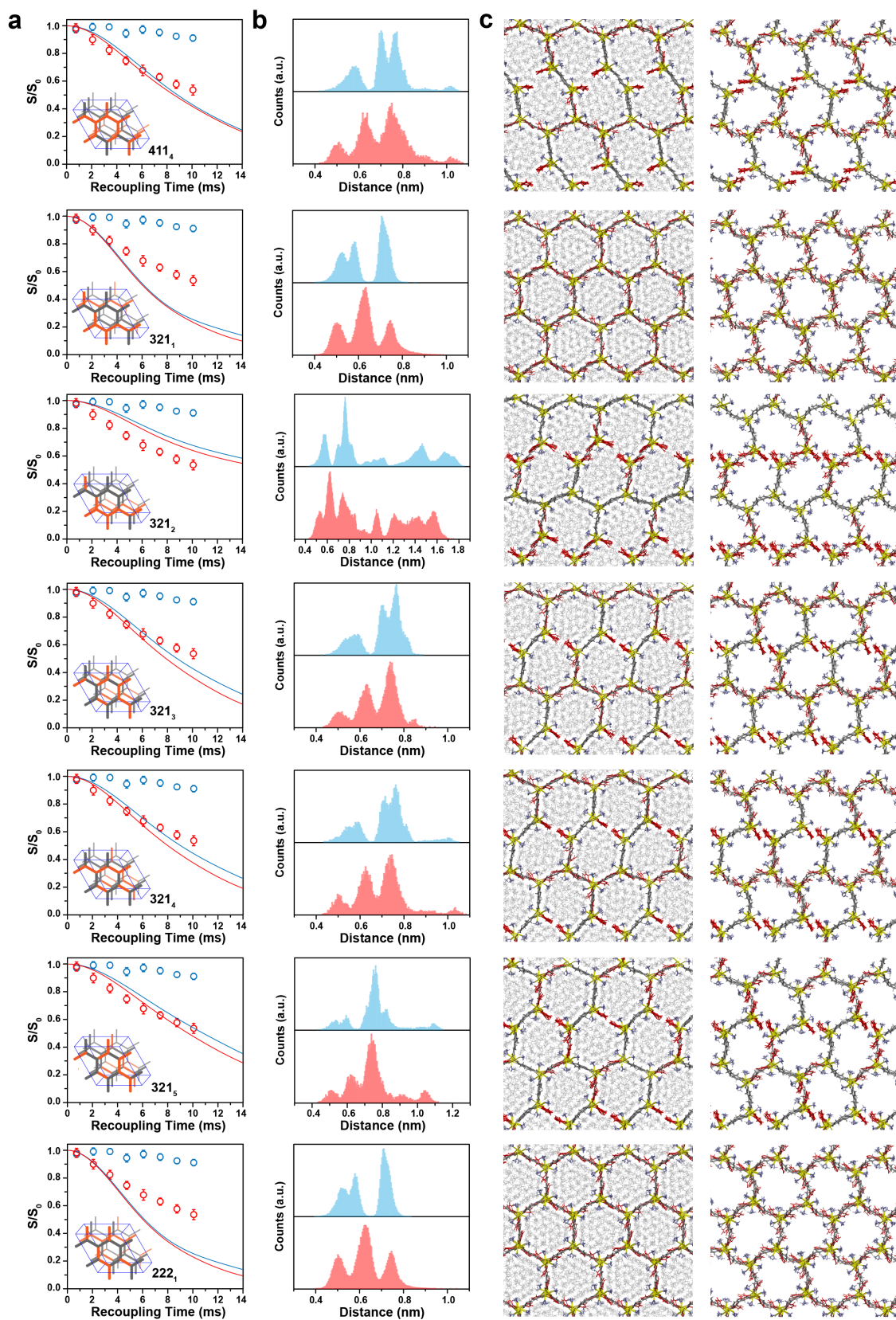


Figure S18. Continued



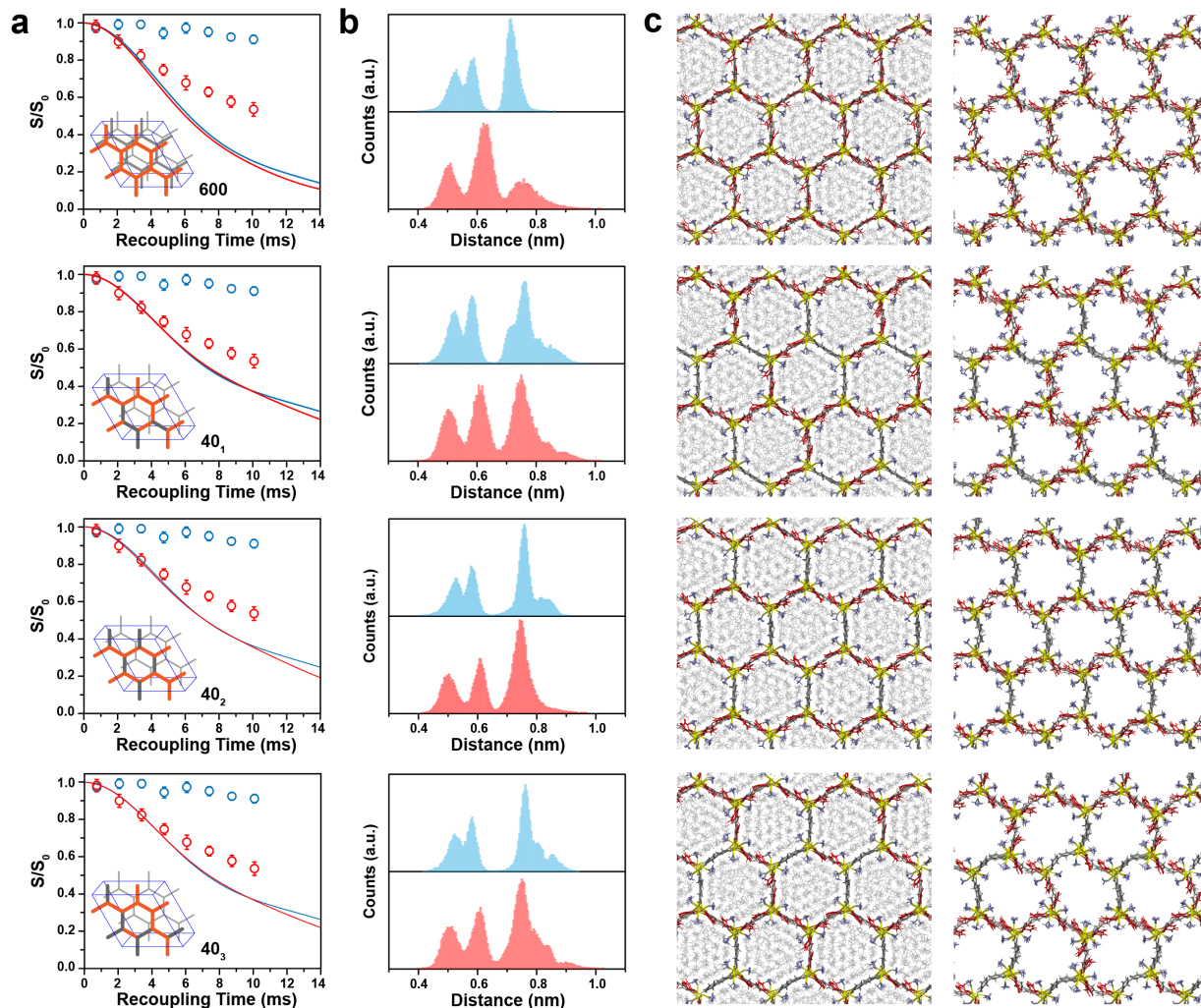


Figure S19. $^{13}\text{C}\{^{19}\text{F}\}$ REDOR investigations for hypothetical **2D planar distributions** of defects in $\text{Mg}_2(\text{dobpdc})$. (a) The simulated REDOR curves for corresponding defect distribution motifs. The blue REDOR curves are for the "wet" sample and the red curves are for the "dry" sample according to the statistical ^{13}C - ^{19}F distances. Experimental REDOR data points are shown as open circles. (b) The simulated distribution of distances between the carbon at 122 ppm (on the dobpdc^{4-} linker) and their nearest F atoms (on the Fs^{2-} ligand) for "wet" (blue) and "dry" (red) conditions. (c) The snapshots of MD optimized superlattices for the "wet" or "dry" samples. Different colored sticks represent different components: red for Fs^{2-} ligands, grey for dobpdc^{4-} linkers, yellow for metal-oxygen atoms, light blue for coordinated methanol and silver for physically adsorbed methanol.

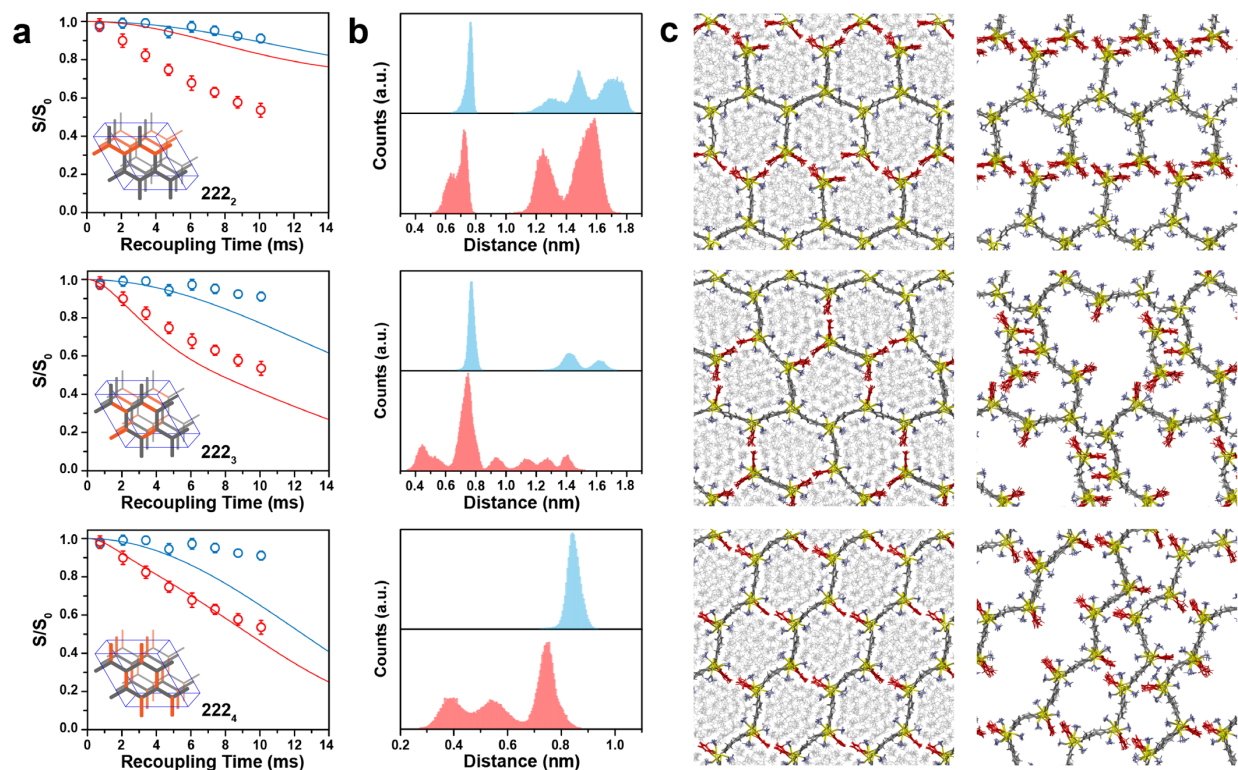


Figure S20. $^{13}\text{C}\{^{19}\text{F}\}$ REDOR investigations for hypothetical **1D alignment** of defects in parallel with the c-axis in $\text{Mg}_2(\text{dobpdc})$. (a) The simulated REDOR curves for corresponding defect distribution motifs. The blue REDOR curves are for the “wet” sample and the red curves are for the “dry” sample according to the statistical ^{13}C - ^{19}F distances. Experimental REDOR data points are shown as open circles. (b) The simulated distribution of distances between the carbon at 122 ppm (on the dobpdc^{4-} linker) and their nearest F atoms (on the Fs^{2-} ligand) for “wet” (blue) and “dry” (red) conditions. (c) The snapshots of MD optimized superlattices for the “wet” or “dry” samples. Different colored sticks represent different components: red for Fs^{2-} ligands, grey for dobpdc^{4-} linkers, yellow for metal-oxygen atoms, light blue for coordinated methanol and silver for physically adsorbed methanol.

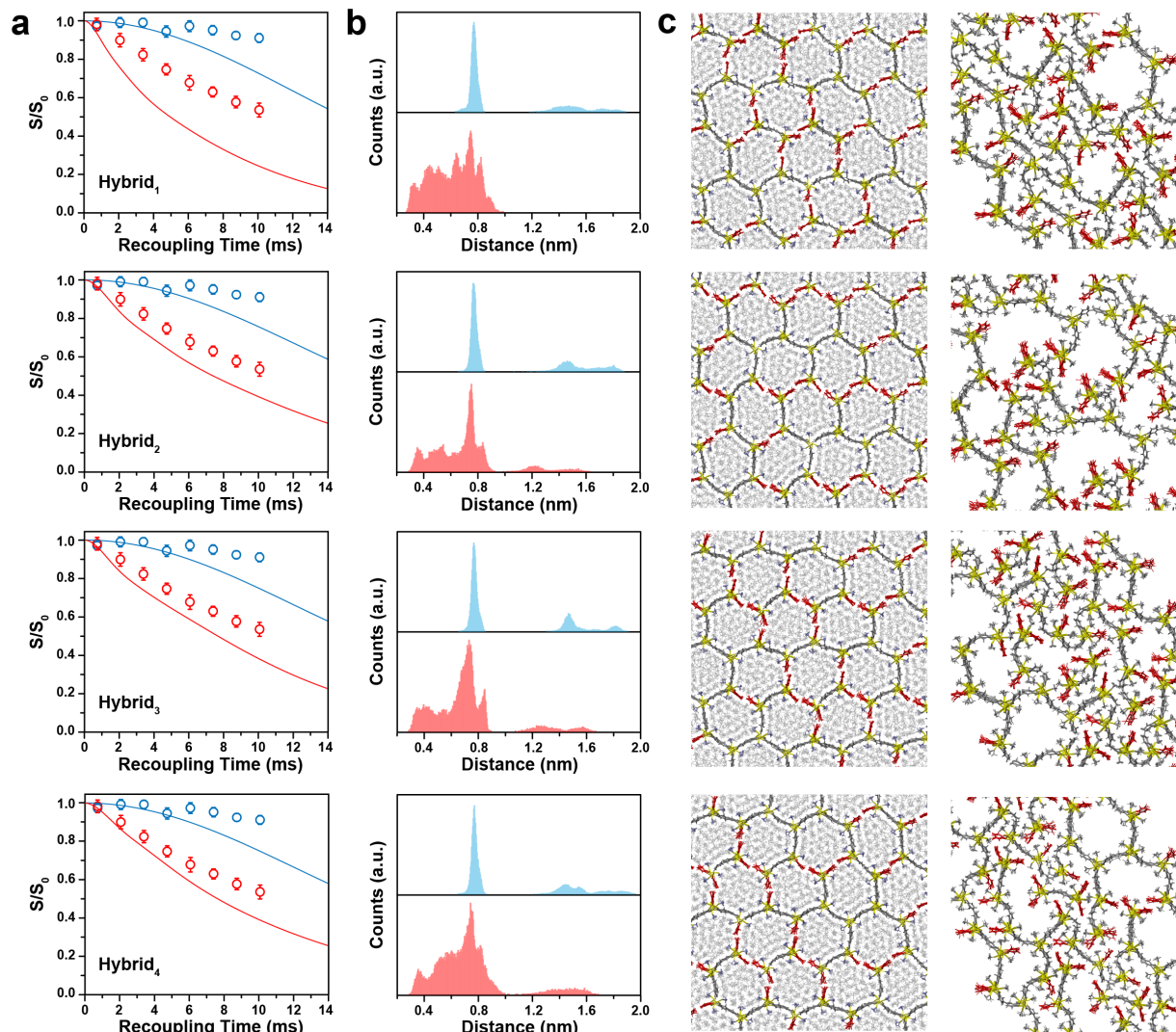


Figure S21. $^{13}\text{C}\{^{19}\text{F}\}$ REDOR investigations of the hypothetical **hybrid structures** consist of a mixture of distribution motifs shown in Fig. S20. These hybrid structures are used for the 1D alignment scenario in Fig. 4. (a) The simulated REDOR curves for the hybrid distribution scenarios. The blue REDOR curves are for the “wet” sample and the red curves are for the “dry” sample according to the statistical ^{13}C - ^{19}F distances. Experimental REDOR data points are shown as open circles. (b) The simulated distribution of distances between the carbon at 122 ppm (on the dobpdc^{4-} linker) and their nearest F atoms (on the Fs^{2-} ligand) for “wet” (blue) and “dry” (red) conditions. (c) The snapshots of MD optimized superlattices for the “wet” or “dry” samples. Different colored sticks represent different components: red for Fs^{2-} ligands, grey for dobpdc^{4-} linkers, yellow for metal-oxygen atoms, light blue for coordinated methanol and silver for physically adsorbed methanol.

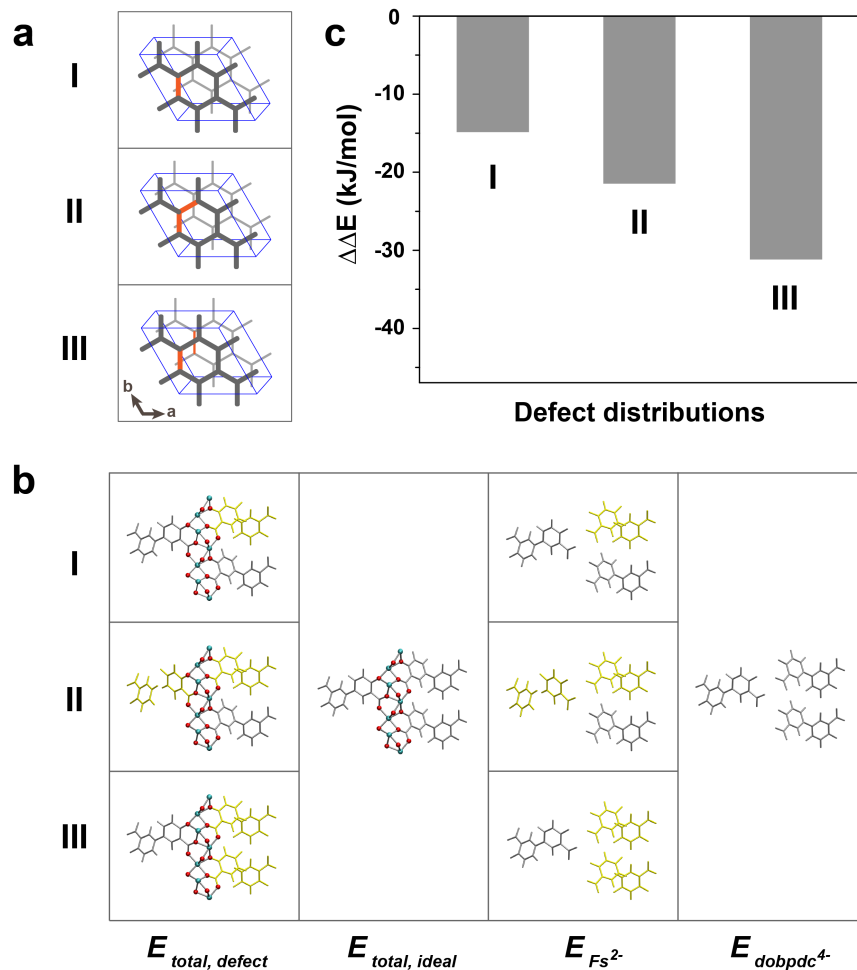


Figure S22 (a) The motifs and (b) the molecular segments for corresponding energy terms used for DFT calculations. Three scenarios are considered: (I) the structure with one edge replaced by a pair of Fs^{2-} ligands; (II) the structure with two edges in the ab plane replaced by two pairs of Fs^{2-} ligands; (III) the structure with two edges along the c -axis replaced by two pairs of Fs^{2-} ligands. (c) The relative energies corresponding to different defect distribution motifs. The structure III is the most stable among the three possible scenarios according to the DFT calculation.

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