Electronic Supplementary Information (ESI):

Insights into the Copolymerization of Metal-Organic Nanotubes from Ligand Mixtures Using Small Angle Neutron Scattering

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I. Experimental Section

General Considerations for Synthesis

The compounds 4,4'-(1,4-(xylene)diyl)bis(1,2,4-triazole) (**L1**) and (**L2**) were prepared as previously described.[1, 2] Dimethylsulfoxide-d_6 was degassed by three freeze-pump-thaw cycles and stored over 4 Å molecular sieves in an N_2 atmosphere prior to use as a deuteron source. All other reagents and solvents were purchased from commercial vendors and used without further purification.

Solution state ^{1}H and ^{13}C NMR spectra were recorded in dimethylsulfoxide-d_6 at 25 °C on a Bruker AVANCE NEO 500 MHz system, and chemical shifts were referenced to the residual solvent.[3] Infrared spectra were collected neat on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance. All mass spectrometry analyses were conducted at the Biological and Mass Spectrometry Core Facility located in the Department of Chemistry at the University of Tennessee-Knoxville. DART analysis was performed using a JEOL AccuTOF-D time-of-flight (TOF) mass spectrometer with a DART (direct analysis in real time) ionization source from JEOL USA, Inc. (Peabody, MA). DART-MS peak areas were calculated as a centroided spectrum and corrected for ^{13}C and ^{15}N natural abundances.[4]

Powder X-ray diffraction data were collected on the samples using a Panalytical Empyrean θ-2θ diffractometer in reflectance Bragg-Brentano geometry. Cu-Kα radiation (λ = 1.5406 Å; 1,800 W, 45 kV, 40 mA) was focused using a planar Gobel Mirror riding the Kα line. A 0.25 mm divergence slit was used for all measurements. Diffracted radiation was detected using a PIXcelz3d detector (3.35° 2θ sampling width) equipped with a Ni monochromator. Each sample was mounted onto a zero-background silicon plate fixed in a sample holder by placing the powdered sample directly onto the plate. Sufficient counting statistics were achieved by using a

0.0394º 2θ step scan from 3 – 50° with an exposure time of 118.30 s per step and a revolution spin rate of 2 s.

Synthesis of 1,3-bis((4*H*-1,2,4-triazol-4-yl-d$_2$)methyl-d$_2$)benzene, L1-*d*$_8$.

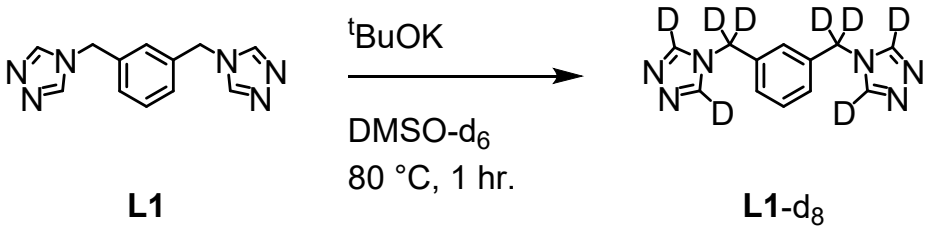

Figure S1. Synthetic scheme for **L1-*d*$_8$**.

1,3-bis((4*H*-1,2,4-triazol-4-yl-d$_2$)methyl-d$_2$)benzene was synthesized by modification of literature procedure.[5] 1.03 g 1,3-bis((4*H*-1,2,4-triazol-4-yl)methyl)benzene was dissolved in 10 mL DMSO-d_6 under N_2 atmosphere. 44.0 mg of potassium *tert*-butoxide was added, and the solution immediately changed from golden-yellow to an intense crimson. After stirring at 80 °C for 1 hour, the vial was removed from the glovebox and quenched with 5 mL of D_2O. The mixture was dried *in vacuo*, the dark orange residue was suspended in 15 mL of $CHCl_3$, filtered, and rinsed with Et_2O to provide a beige powder. (911 mg, 86.2% as MW_{avg} = 246.07 g/mol). A second repetition of this procedure with the initial product showed additional enrichment (MW_{avg} = 247.22 g/mol). Further repetitions did not show substantial additional enrichment with this procedure.

^{1}H NMR (500.21 MHz, DMSO-d_6) d <u>8.57</u> (s, 0.06H), 7.39 (t, J = 7.7 Hz, 1H), 7.28 (t, J = 1.8 Hz, 1H), 7.24 (dd, J = 7.6, 1.8 Hz, 2H), <u>5.25</u> (s, 0.07H) [*Note*: <u>underlined</u> signals are resonances at deuterated positions]. MW_{avg} = 247.28 g/mol with 1,3,5-trimethoxybenzene as external standard.

^{13}C{^{1}H} NMR (125.79 MHz, DMSO-d_6) d **142.92** (t, J = 32.1 Hz) 137.18, 129.40, 127.39, 127.03, **46.77** (qt, J = 21.7 Hz) [*Note*: **bold** signals are resonances at deuterated positions].

IR (neat): 3090, **2305**, **2249**, 1609, 1520, 1502, 1471, 1428, 1406, 1317, 1260, 1185, 1165, 1106, 1045, 1036, 982, 952, 913, 847, 786, 762, 750, 726, 700, 651, 628 cm^{-1} [*Note*: **bold** signals arise from C-D vibrational modes].

Sample preparation for SANS Experiment

Stock solutions were prepared by dissolving 6.3, 4.5, and 4.5 mg of **L1**, **L1-*d*$_8$**, and **L2** in 2.87 (9.1 mM), 1.98 (9.2 mM), and 1.95 (9.1 mM) mL dimethylformamide-d_7 (DMF-d_7), respectively, in separate 4 mL vials. Aliquots of each were combined according to the table below (*Note*: Vials 5 and 9 were prepared at 600 µL total due to larger sample cells).

Table S1. Aliquots of **L1**, **L1-*d*$_8$** and **L2** mixtures were prepared for SANS experiments.

	Vial 1	Vial 2	Vial 3	Vial 4	Vial 5*	Vial 6	Vial 7	Vial 8	Vial 9*
volume **L1** (µL)	200	140	100	60	0	400	320	240	240
volume **L1-d$_8$** (µL)	0	60	100	140	300	0	80	160	360
volume **L2** (µL)	200	200	200	200	300	0	0	0	0

Separately, a stock solution of 32.7 mg $CuBr_2$ in 4.00 mL D_2O (36.6 mM) was prepared. Before adding the reagents, the banjo cells (used for SANS measurements), were heated at 85 °C for 10 minutes. The vials containing $CuBr_2$ solution and ligand mixtures were also heated at 85 °C for 3-5 minutes. 200 µL of $CuBr_2$ solution (Vials 5 and 9: 300 µL) was transferred to the banjo

cell, followed by adding 400 µL of ligand mixture (Vials 5 and 9: 600 µL) in approximately 80 µL aliquots. Between each aliquot, the banjo cell was gently shaken to remove any bubbles.

MONT Acid Digestion and ^{1}H NMR

Bulk MONT synthesis: Stock solutions of **L1** (72.1 mg in 8.00 mL DMF, 37.5 mM), **L1-*d*$_8$** (26.8 mg in 2.90 mL DMF, 37.5 mM), **L2** (76.3 mg in 8.00 mL DMF, 37.5 mM), and $CuBr_2$ (335.0 mg in 10.00 mL H_2O, 150 mM) were prepared. The ligand solutions were heated at 85 °C for 30 minutes to aid dissolution. After dissolution, stock solutions were cooled, combined in separate 4 mL vials, sealed, and swirled to mix as in Table S2. After mixing, 510 µL of $CuBr_2$ (preheated to 85 °C for 15 minutes) were added to each vial (also preheated to 85 °C for 15 minutes). The vials were immediately sealed, swirled to mix, and placed in an aluminum heating block pre-heated to 85 °C for 7 days.

Table S2. Aliquots of **L1**, **L1-*d*$_8$** and **L2** mixtures were prepared for SANS experiments.

L1 : **L1-*d*$_8$** : **L2**	50 : 0 : 50	35 : 15 : 50	25 : 25 : 50	15 : 35 : 50	0 : 50 : 50
volume **L1** (µL)	510	357	255	153	0
volume **L1-*d*$_8$** (µL)	0	153	255	357	510
volume **L2** (µL)	510	510	510	510	510

Acid digestion procedure: Approximately 5 mg dried MONT and 250 µL 35% DCl in D_2O were combined in a vial. The vial was swirled to mix, sealed, and allowed to react at room temperature for 5 minutes (dissolution completed within 2 minutes). The yellow solution was neutralized by adding solid K_2CO_3 until effervescence ceased, then an additional 10 mg were added. The light

blue suspension was filtered through oven-dried Celite and the solids were washed with 500 µL DMSO-d_6. The ^{1}H NMR spectrum of the resulting colorless solution was then collected and the methylene positions (5.27 ppm in **L1** and 5.22 ppm in **L2**) with the benzylic CH_3 (2.27 ppm in **L2**) functioning as an internal standard.

Powder X-ray Diffraction Experiments

Stock solutions were prepared by dissolving 147.9 mg **L1** in 16.40 mL DMF and 153.4 mg **L2** in 16.40 mL DMF in separate vials. Each vial was sealed, swirled to mix, and heated at 60 °C until dissolved, then cooled to room temperature. In separate 4 mL vials, aliquots of **L1** and **L2** stock solution were combined as described in table **S3**, then sealed and swirled to mix.

Table S3. Aliquots of **L1**, **L1-*d*$_8$** and **L2** mixtures were prepared for SANS experiments.

L1 : **L2**	100 : 0	75 : 25	50 : 50	25 : 75	0 : 100
volume **L1** (µL)	2000	1500	1000	500	0
volume **L2** (µL)	0	500	1000	1500	2000

After mixing, each vial was heated to 85 °C for 15 minutes, then 1000 µL $CuBr_2$ solution (552.8 mg in 10.0 mL H_2O, 150 mM), also pre-heated for 15 minutes at 85 °C, were added to each vial. All vials sealed, swirled to mix, and heated in an aluminum heating block at 85 °C for 7 days. The contents of each vial was then filtered, washed sequentially with 3 × 1 mL rinses H_2O, 3×1 mL rinses acetone, and 3 × 1 mL rinses Et_2O and allowed to dry. Separately, approximately 5 mg each of **L1** MONT and **L2** MOF were combined to serve as a sample of a discrete phase material. All

samples were lightly ground in a mortar and pestle prior to powder X-ray diffraction experiments.

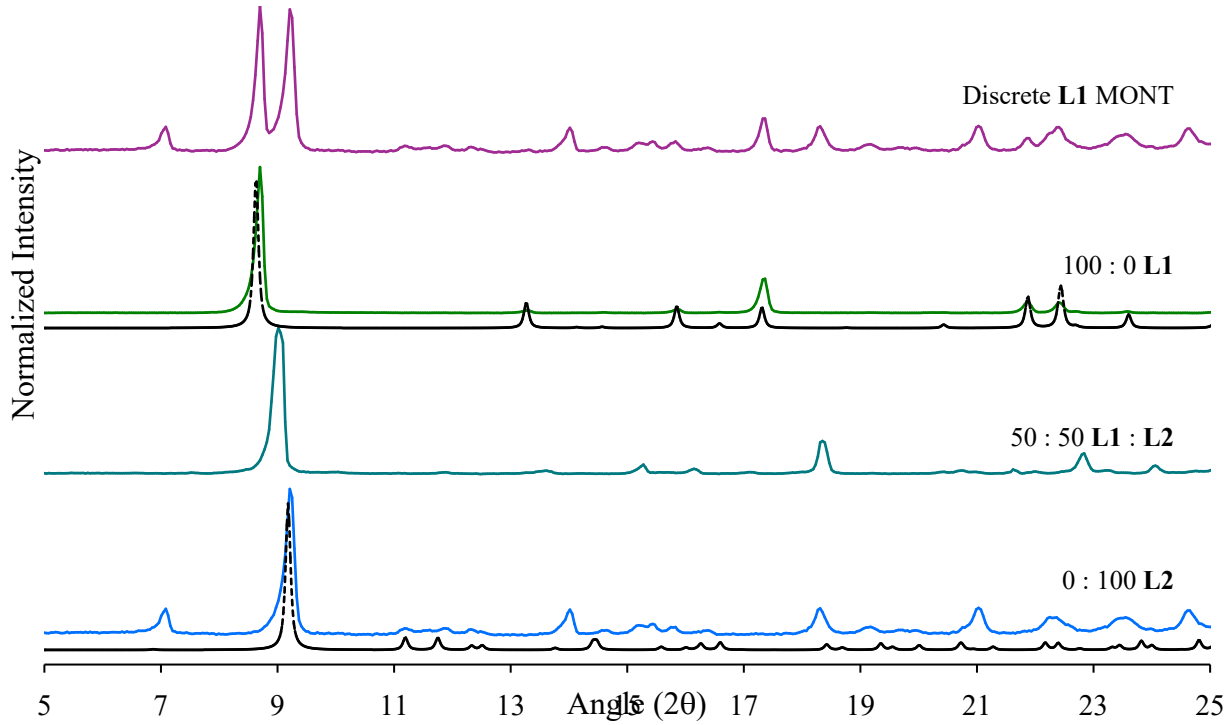

Figure S2. Powder X-ray diffraction data of **L1** MONT (green, 2nd from top), 50:50 **L1** : **L2** (teal, 3rd from top), and **L2** MOF (bottom, blue), compared to a post-synthetically mixed **L1** MONT and **L2** MOF (purple, top). Simulated patterns of **L1** MONT and **L2** MOF, generated from previously published data, are included as dashed lines under the corresponding experimental data.[1, 2]

II. Model Used for Fitting Sans Scattering Profile

A combination of two models, parallelepiped and lamellar is used to fit the all the SANS scattering profiles documented in this study.

The scattering intensity from the form factor of the parallelepiped can b e given by the following equation:

$$I(q) = \frac{Scale}{V}(\Delta\rho \,.\, V)^2 \langle P\,(q,\alpha,\beta)\rangle + background$$ **Equation S1**

In Equation S1, V is the volume of the parallelepiped shaped particle, Δρ is the difference between the scattering length density of the particle and solvent. The form factor P (q,α,β) can be expanded using the following Equation S2

$$P(q,\alpha) = \int_0^1 \phi_Q\left(\mu\sqrt{1-\sigma^2}, a\right)\left[S\left(\frac{\mu c\sigma}{2}\right)\right]^2 d\sigma$$ **Equation S2**

Using $\sigma = \cos\alpha$ and $\beta = \frac{\pi}{2}$ u,

$$\phi_Q(\mu,a) = \int_0^1 \left\{S\left[\frac{\mu}{2}cos(\frac{\pi}{2}u)\right] S\left[\frac{\mu a}{2}\sin(\frac{\pi}{2}u)\right]\right\}^2 du$$

$$S(x) = \frac{sinx}{x}$$

$$\mu = qB$$

The scattering intensity of infinitely large lamellae is defined by the following equation

$$I(q) = scale\,\frac{2\pi\,P(q)}{q^2\delta} + background$$ **Equation S3**

P(q) in equation S3 can be expanded using the following equation

$$P(q) = \frac{2\,\Delta\rho^2}{q^2}(1 - \cos(q\delta))$$ **Equation S4**

Here, δ is the total layer thickness and Δρ is the difference between the scattering length density of the particle and solvent.

III. Selected Spectra and other Analytical Data

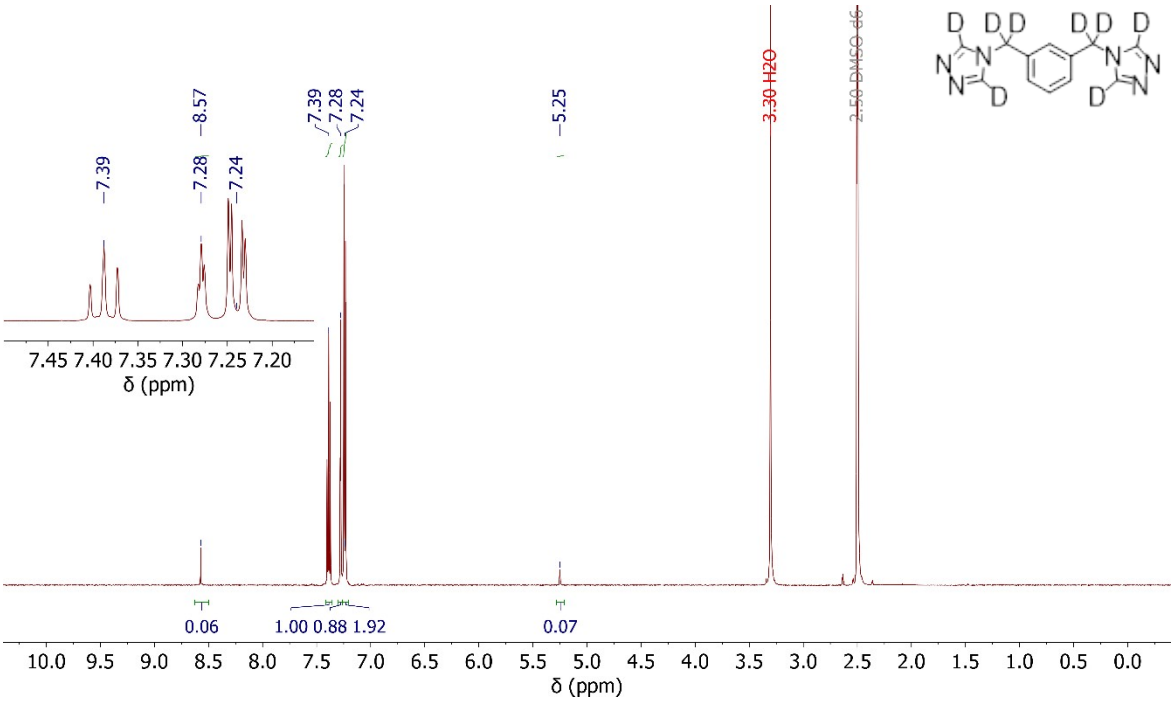

Figure S3. ^{1}H NMR of **L1-*d*$_8$** in DMSO-d_6. Peaks at 8.57 and 5.25 pm align with **L1**[1] triazole and methylene positions, respectively.

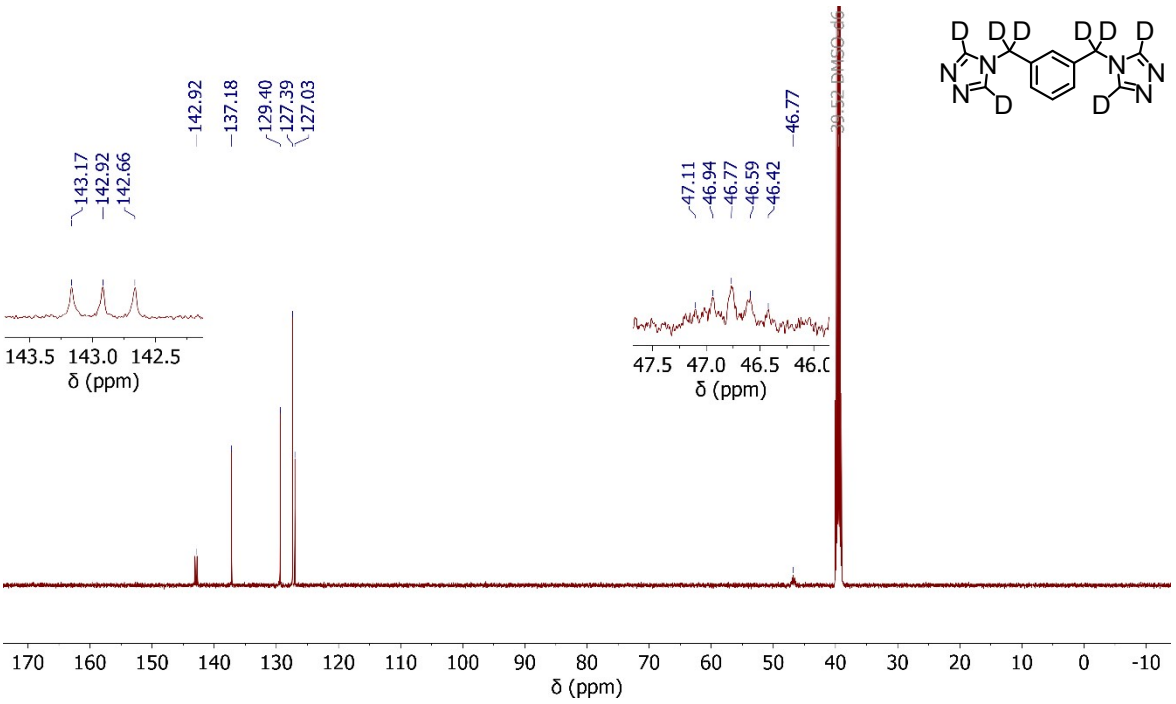

Figure S4. $^{13}C\{^{1}H\}$ NMR of **L1-*d*$_8$** in DMSO-d_6. The triplet observed at 142.92 ppm is slightly upfield with regards to the triazole ^{13}C resonance of **L1** (143.22 ppm)[1] indicating symmetric deuteration at the triazole 3- and 5- position with ^{13}C split by a single deuteron. The signal at 46.77 ppm is similarly upfield with respect to **L1** (47.32 ppm in **L1**[1]) and split by two deuterons.

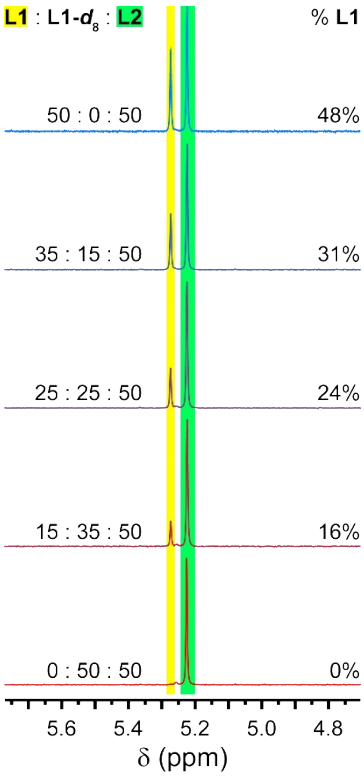

Figure S5. ^{1}H NMR of post-synthetically digested **L1** : **L1-*d*$_8$** : **L2** in DMSO-d_6, centered at the methylene signals of **L1** and **L2** with the benzylic protons of **L2** as an internal standard. The initial reaction ratios, shown left of signals, and the integrated area of **L1** (highlighted in yellow) and **L2** (highlighted in green), shown on the right, show excellent agreement.

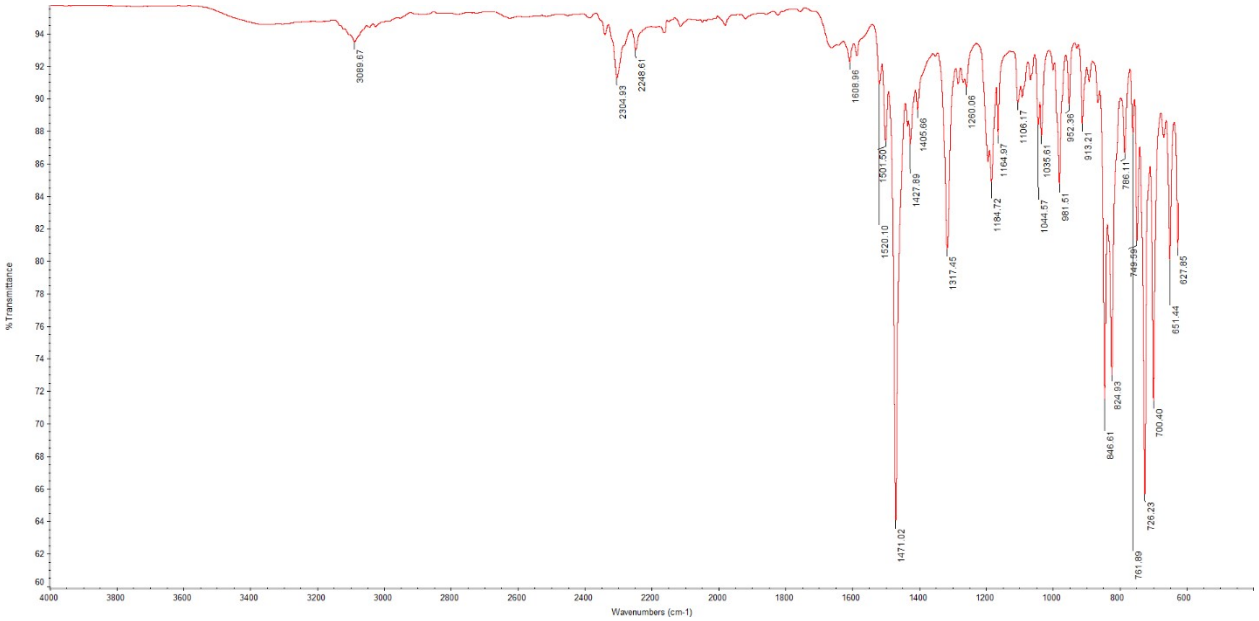

Figure S6. ATR-IR spectrum of **L1-*d*$_8$**. Signals at 2305 and 2249 cm^{-1} correspond to C-D vibrations.

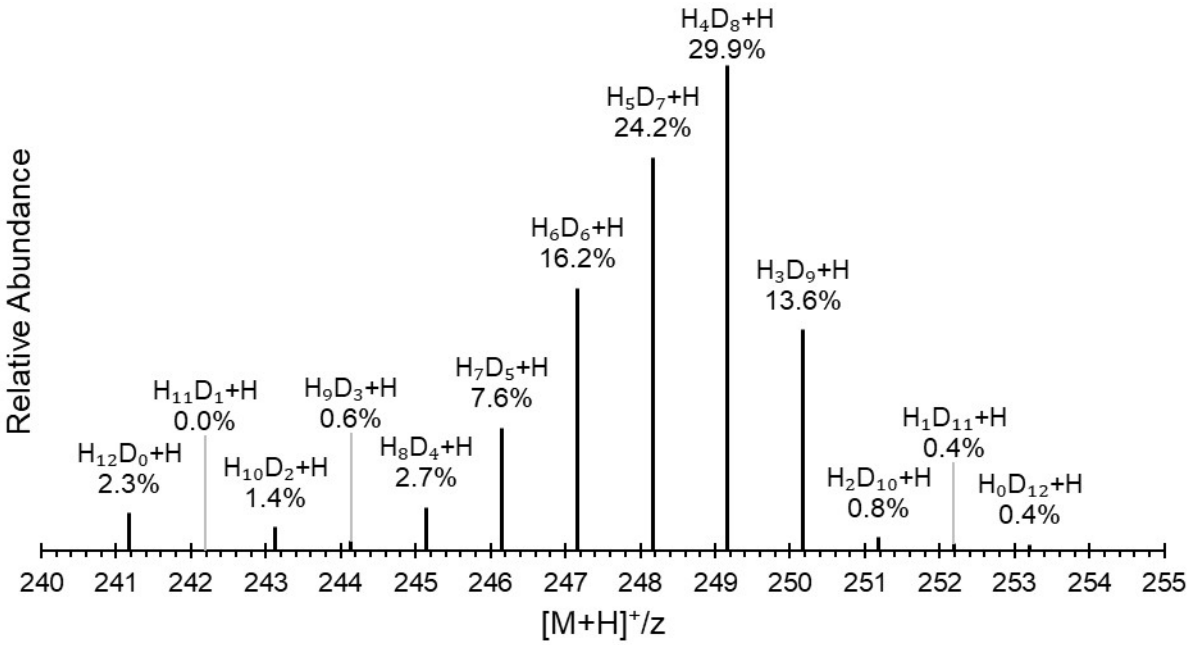

Figure S7. High-resolution DART-MS of **L1-*d*$_8$** with labels of percentage of deuteration at each $[M+H]^+$.

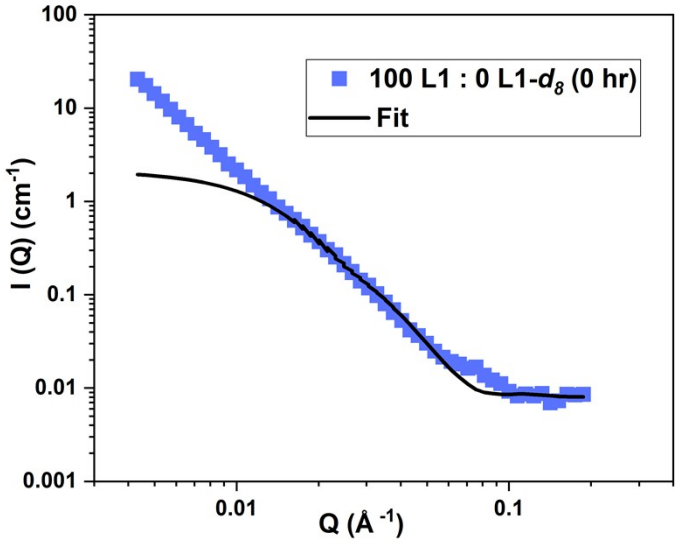

Figure S8. A demonstration of the parallelepiped model failing to fit the SANS scattering profile of nanostructure formed from 100 **L1** : 0 **L1-*d*$_8$**.

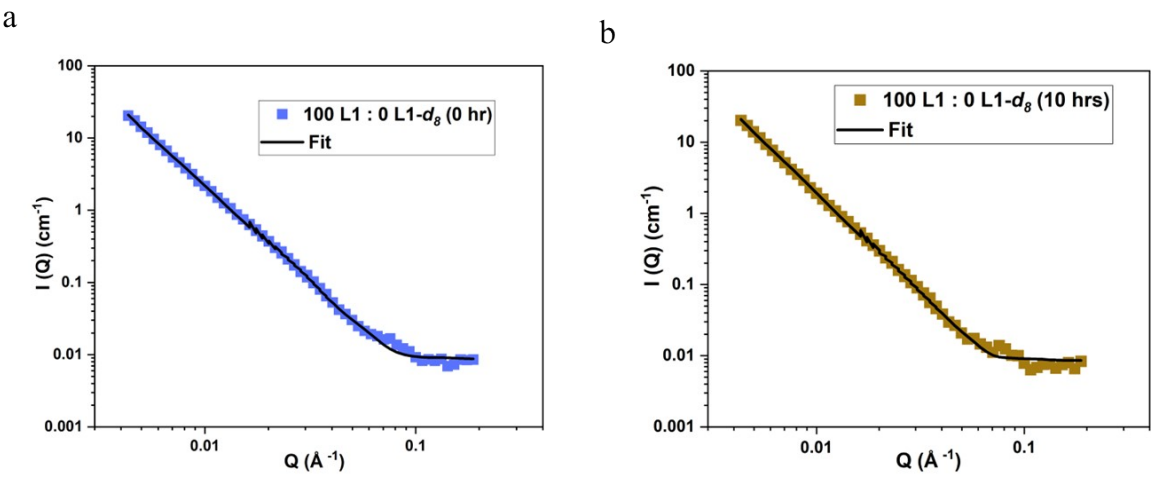

Figure S9. SANS scattering profile fit of 100 **L1** : 0 **L1-d_8** using the combined model of lamellar and parallelepiped at indicated reaction times.

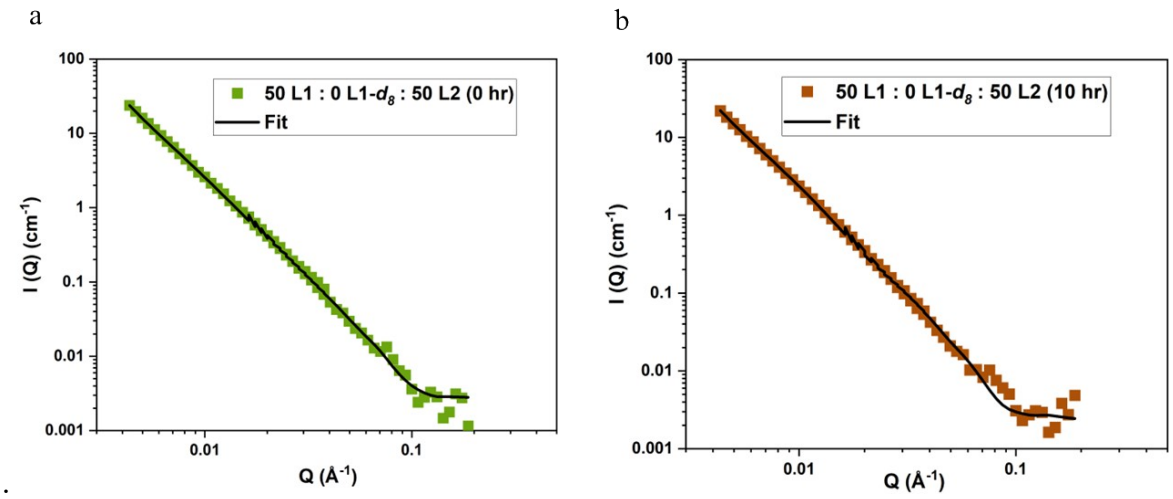

Figure S10. SANS scattering profile fit of 50 **L1**: 0 **L1-d_8** : 50 **L2** using the combined model of lamellar and parallelepiped at indicated reaction times.

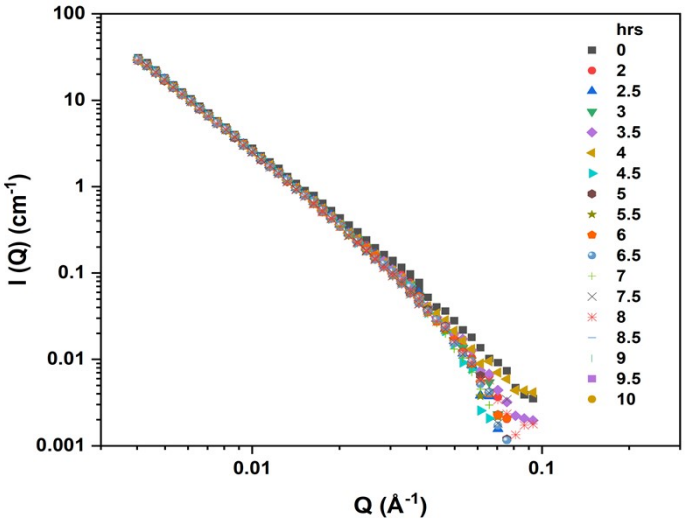

Figure S11. SANS scattering profile of 50 **L1**: 0 **L1-d_8** : 50 **L2** at indicated reaction times.

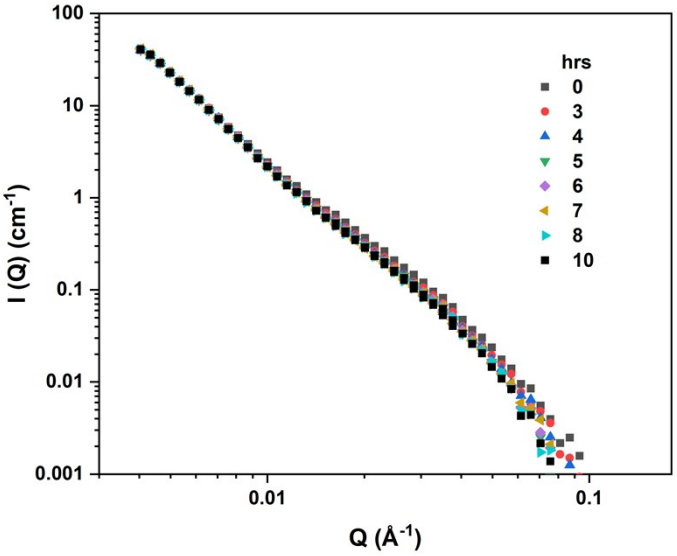

Figure S12. SANS scattering profile of 35 **L1**:15 **L1-*d*$_8$** : 50 **L2** at indicated reaction times.

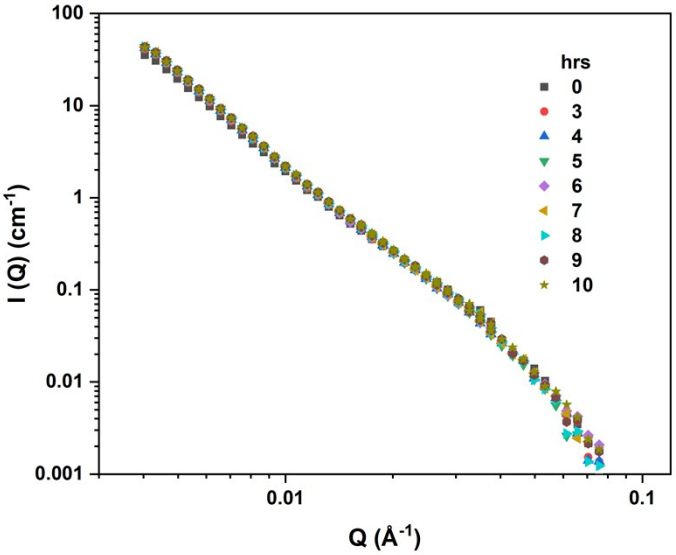

Figure S13. SANS scattering profile of 25 **L1**:25 **L1-*d*$_8$** : 50 **L2** at indicated reaction times.

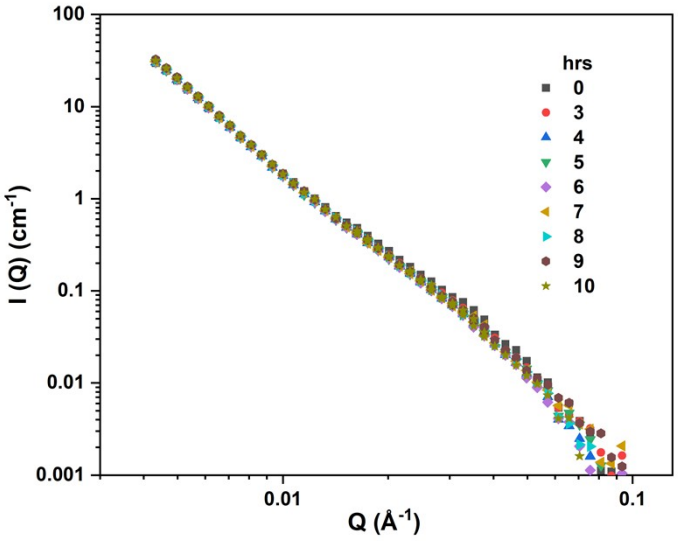

Figure S14. SANS scattering profile of 15 **L1**:35 **L1-*d*$_8$** : 50 **L2** at indicated reaction times.

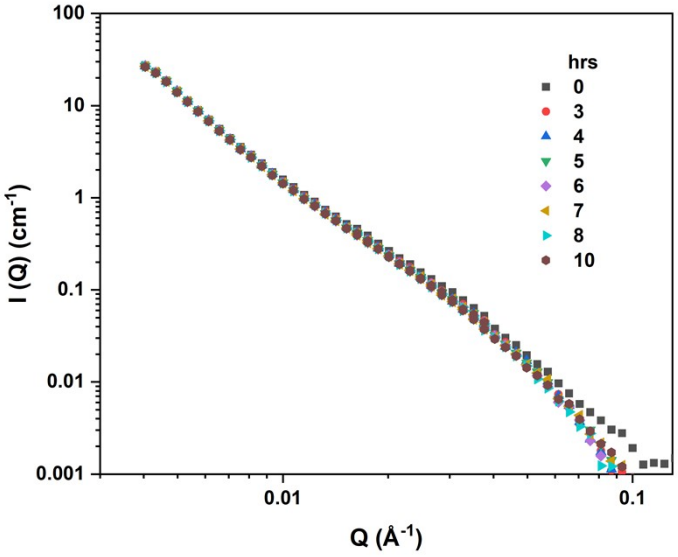

Figure S15. SANS scattering profile of 0 **L1**:50 **L1-*d*$_8$** : 50 **L2** at indicated reaction times.

Table S4. Scattering length densities (SLDs) obtained from the fitting of scattering profile of **L1** and **L1-*d*$_8$** mixture at ratio of 100:0, 80:20, 40:60 and 60:40

L1 : **L1-*d*$_8$**	SLD (Lamellae) 0 hr	SLD (Lamellae) 10 hrs	SLD (Parallelepiped) 0 hr	SLD (Parallelepiped) 10 hr
100:0	4.20	4.56	4.12	4.45
80:20	4.43	4.73	4.33	4.63
60:40	4.64	4.91	4.55	4.79
40:60	4.85	5.07	4.79	5.00

Table S5. Scattering length densities (SLDs) obtained from the fitting of scattering profile of **L1**, **L1-*d*$_8$, L2** and mixture at ratio of 50:0:50, 35:15:50, 25:25:50, 15:35:50, 0:50:50.

L1 : **L1-*d*$_8$** : **L2**	SLD (Lamellae) 0 hr	SLD (Lamellae) 10 hrs	SLD (Parallelepiped) 0 hr	SLD (Parallelepiped) 10 hr
50:0:50	4.20	4.54	4.00	4.18
35:15:50	4.38	4.67	4.20	4.33
25:25:50	4.48	4.75	4.32	4.46
15:35:50	4.58	4.83	4.43	4.55
0:50:50	4.74	4.96	4.56	4.73

Table S6. Polydispersity of lamellae formed from the mixture of **L1** and **L1-*d*$_8$**

L1 : **L1-d_8**	Polydispersity (Lamellae) 0 hr	Polydispersity (Lamellae) 10 hrs
100:0	0.52	0.33
80:20	0.94	0.83
60:40	0.94	0.87
40:60	0.96	0.76

Table S7. Polydispersity of lamellae formed from the mixture of **L1**, **L1-d_8** and **L2**.

L1 : **L1-d_8** : **L2**	Polydispersity (Lamellae) 0 hr	Polydispersity (Lamellae) 10 hrs
50:0:50	0.63	0.25
35:15:50	0.94	0.64
25:25:50	0.94	0.51
15:35:50	0.94	0.67
0:50:50	0.94	0.80

IV. References

1. Murdock, C. R.; Jenkins, D. M. Isostructural Synthesis of Porous Metal–Organic Nanotubes. *Journal of the American Chemical Society* **2014**, *136* (31), 10983-10988.
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