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Supporting Information

Intermediate Single Crystal Trapping of COF-300 via Organic Lewis Acid Catalysis

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1. General considerations

1.1 Instruments

Single-crystal X-ray diffraction data were collected using a Bruker D8 Venture X-ray single-crystal diffractometer with Metaljet. The APEX IV (v2022.10-0) software was used to collect (by SAINT V8.40 A) and refine (by SADABS V2.03 and SHELXT V2018/2) the diffraction data. Crystal structures were solved using the direct method with the Olex 2 (V1.5) software, and data were corrected using the built-in SHELXL program (V2014-3) through the full-matrix least-squares method. All nonhydrogen atoms were treated anisotropically, while hydrogen atoms were determined from electron density or theoretical hydrogenation.

Powder X-ray diffraction (PXRD) patterns were collected on a SmartLab 9KW desktop X-Ray diffractometer operated at 30 kV and 15 mA (step = 0.01°, scan rate = 3°/min).

Fourier Transform Infrared (FT-IR) spectra were recorded on a ThermoFisher-6700.

Scanning Electron Microscopy (SEM) images were recorded with a Hitachi SU5000 scanning electron microscope.

Thermogravimetric analysis (TGA) measurements were performed on a TA Q600 instrument. The samples were heated from room temperature to 800 °C under N_2 flow (25 ml min^{-1}) at a heating rate of 10 K min^{-1}.

N_2 sorption measurements were performed using an Autosorb-IQ-MP/XR Automated Gas Sorption Analyzer. Nitrogen sorption isotherms were collected at 77 K after vacuum activation of the samples at 120 °C overnight.

1.2 Materials and Reagents.

All chemicals were purchased from Innochem and used without further purification.

2. Synthesis

Synthesis of COF-300 (dia-7):

Tetrakis(4-aminophenyl)methane (TAM, 13 mg, 0.034 mmol), Benzene-1,4-dicarboxaldehyde (BDA, 12 mg, 0.089 mmol), and tris(pentafluorophenyl)borane (16 mg, 0.031 mmol) were added to a 20 mL glass vial. Subsequently, 2 mL of a mixed solvent (1,4-dioxane/mesitylene, 0.5 mL/1.5 mL) was introduced into the vial. After thorough mixing, the vial was placed in an oven and heated at 60 °C for 72 h. Afterwards, the COF solid was filtered off and rinsed thoroughly with THF, acetone, and methanol. The powder was dried under vacuum at 60 °C.

Synthesis of SIM-300:

Tetrakis(4-aminophenyl)methane (TAM, 13 mg, 0.034 mmol), Benzene-1,4-dicarboxaldehyde (BDA, 12 mg, 0.089 mmol), and tris(pentafluorophenyl)borane (16 mg, 0.031 mmol) were added to a 20 mL glass vial. Subsequently, 2 mL of a mixed solvent (1,4-dioxane/mesitylene, 0.5 mL/1.5 mL) was introduced into the vial. After thorough mixing, the vial was placed in an oven and heated at 60 °C for 24 hours, followed by standing undisturbed at 30 °C for 72 h. Afterwards, the solid was filtered off and rinsed thoroughly with THF, acetone, and methanol. The powder was dried under vacuum at 60 °C.

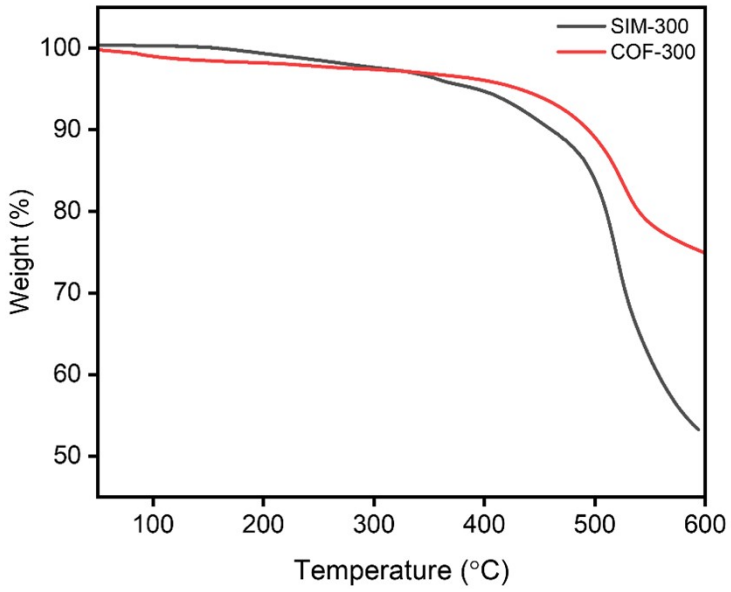

Figure S1. TGA traces of SIM-300 and COF-300.

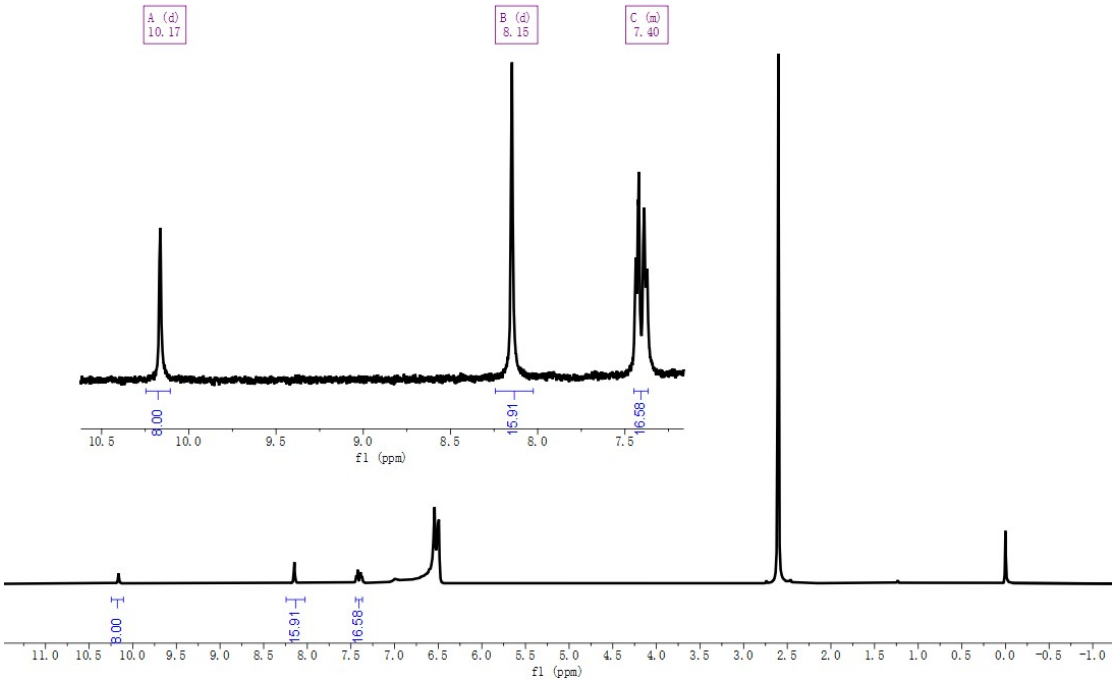

Figure S2. The ^{1}H NMR Spectrum of SIM-300 after acid hydrolysis with DCl in DMSO-d_6. Peaks at δ = 10.17 and 8.15 ppm correspond to the aldehyde proton and aromatic protons of DBA, while the peak at δ = 7.41 ppm is attributed to aromatic protons from the benzene ring of TAM. The ratio of TAM/BDA is ca. 1/4 calculated from the corresponding peak integrals.

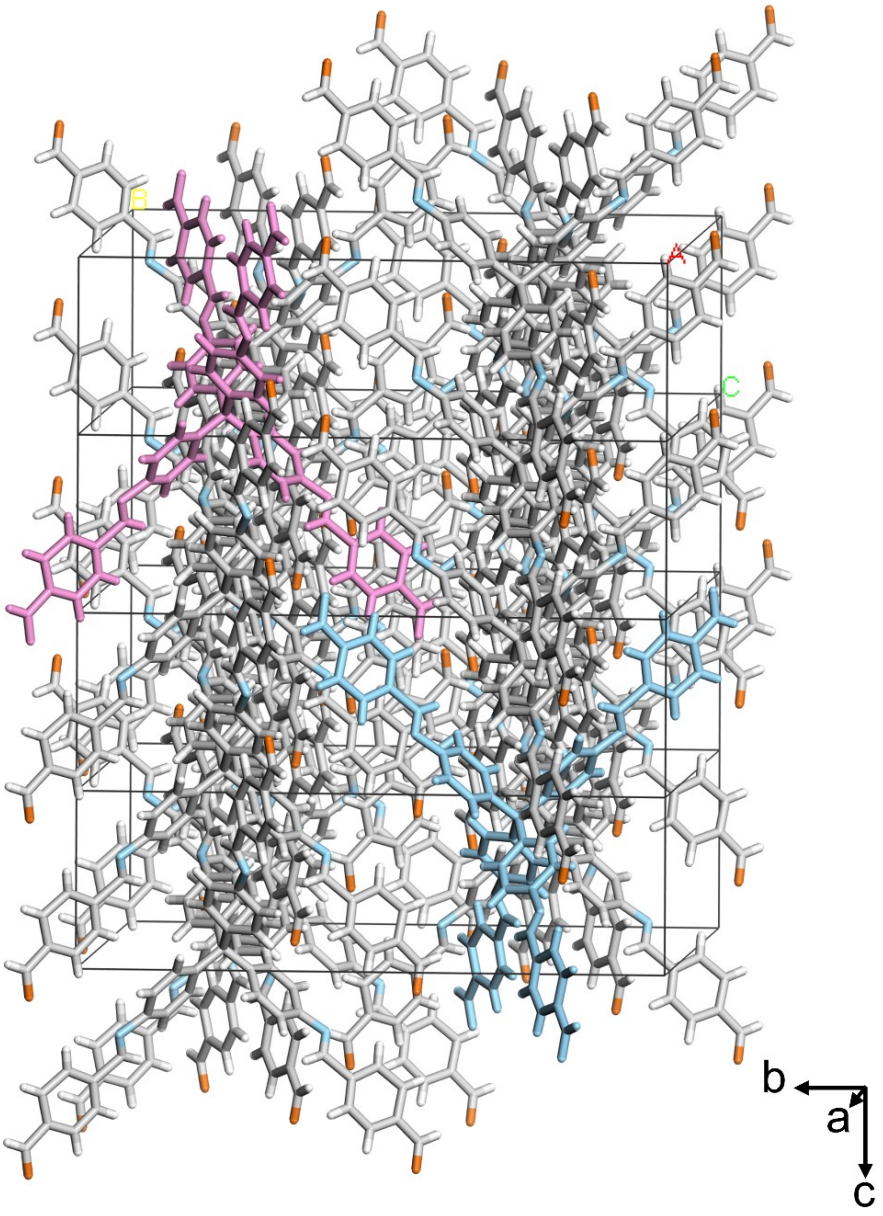

Figure S3. Schematic illustration of the pair of oligomer (blue and purple) to be bonded to form COF-300 from SIM-300.

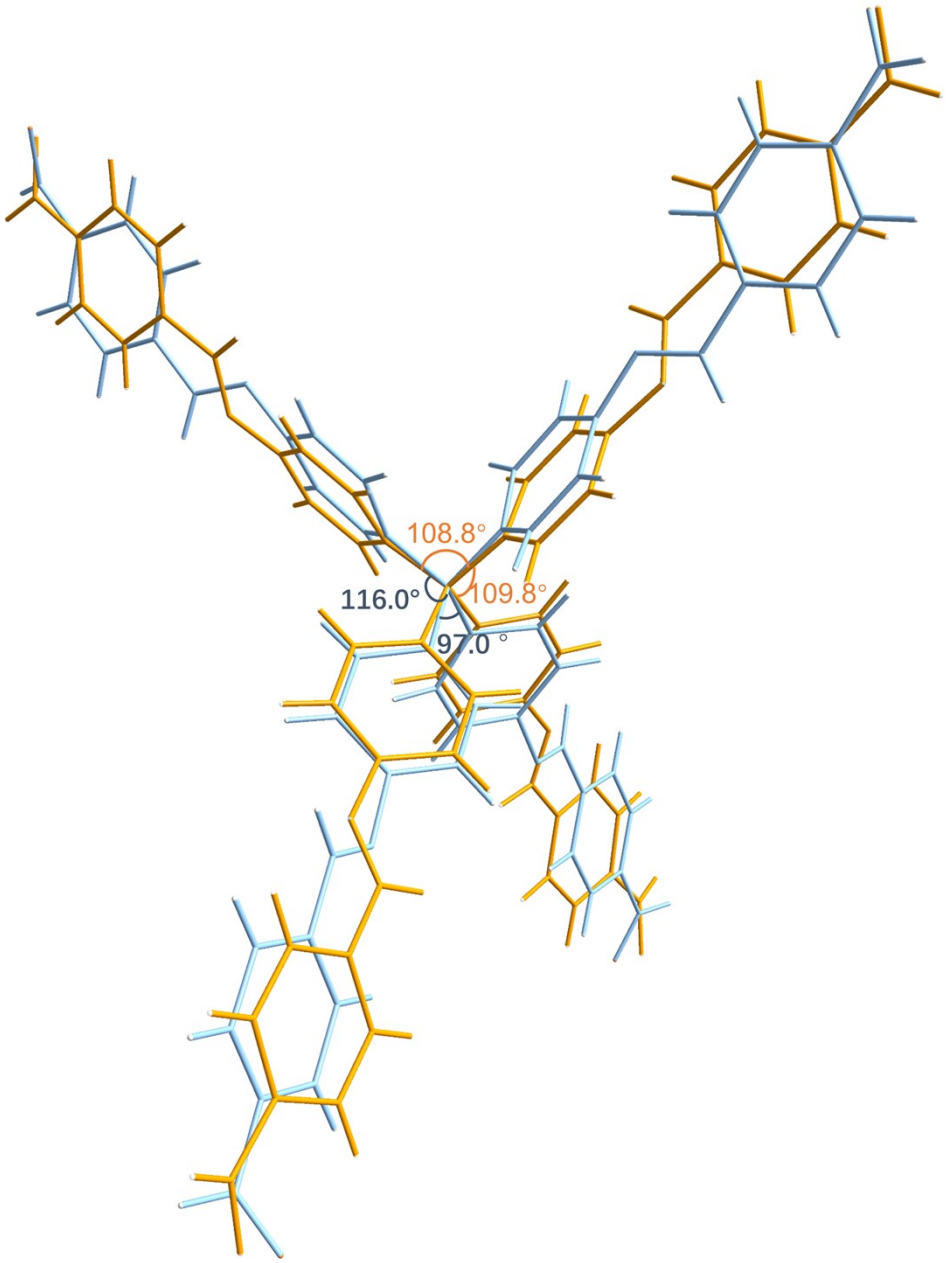

Figure S4. The angles of SIM-300.

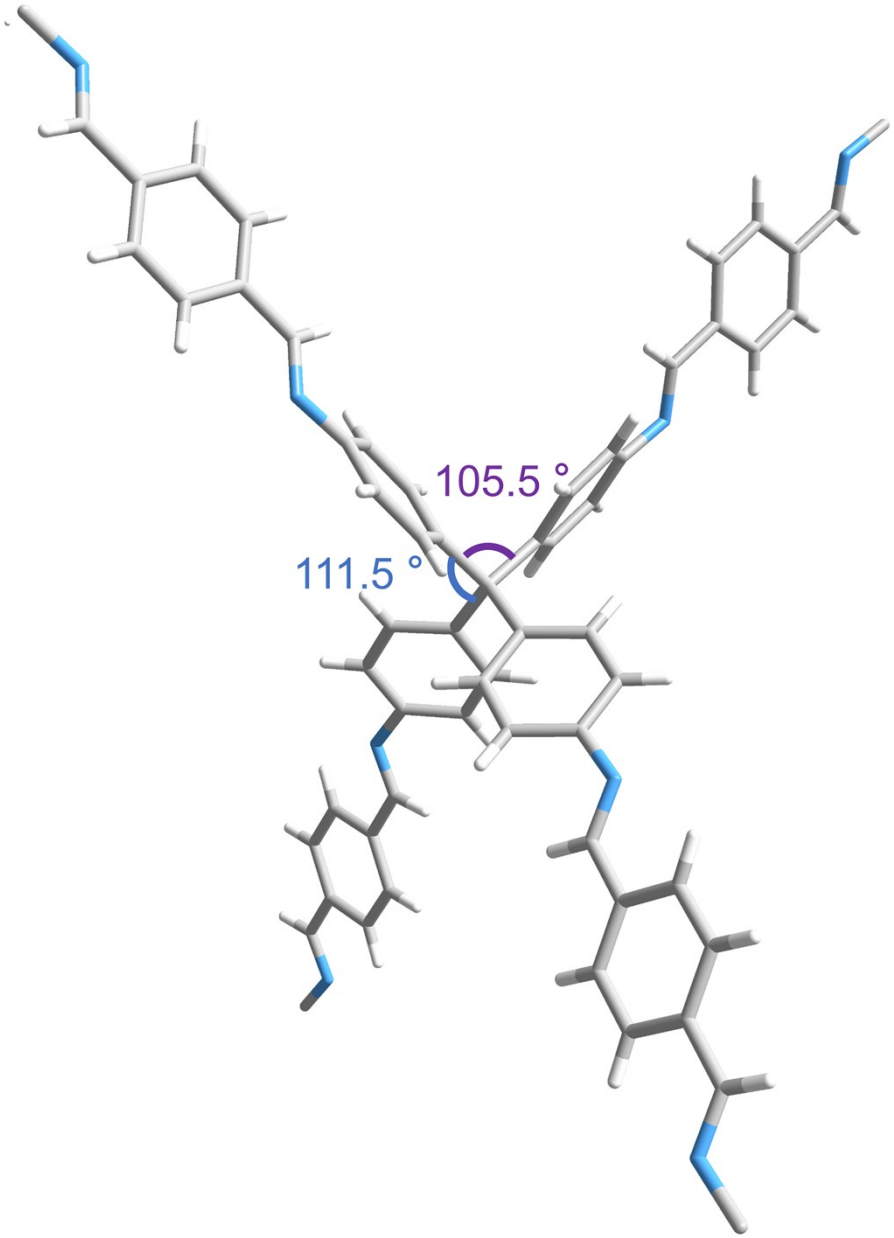

Figure S5. The angles of COF-300.

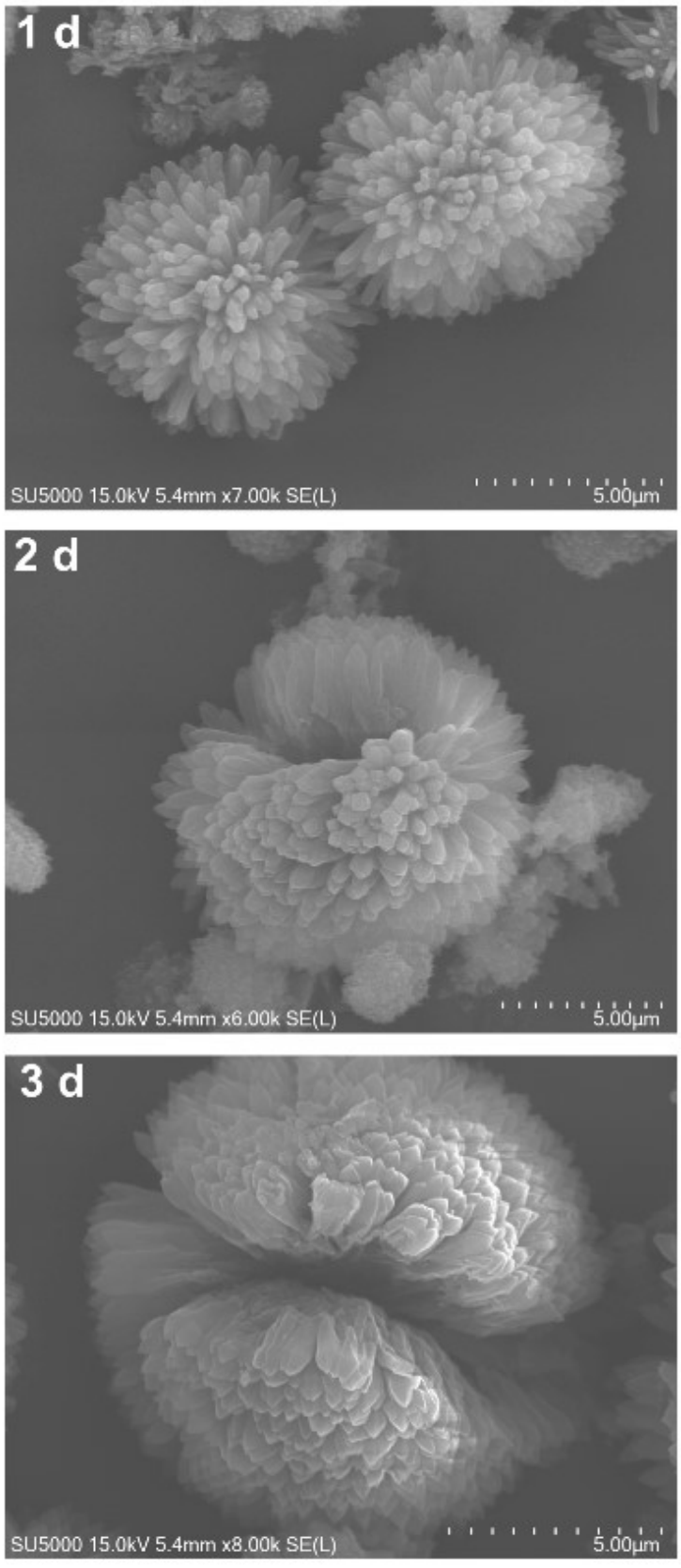

Figure S6. SEM images of solid precipitates at different time intervals during the synthesis of COF-300.

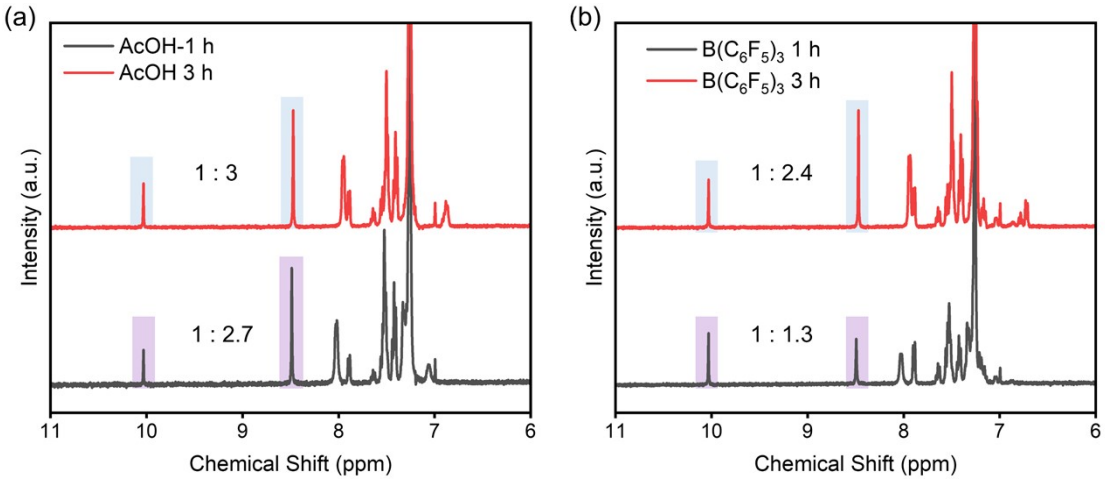

Figure S7. Reaction progress was monitored by liquid-state NMR for model reactions catalyzed by (a) acetic acid and (b) $B(C_6F_5)_3$. The signal at 10.03 ppm is attributed to benzaldehyde, whereas the signal at 8.47 ppm is assigned to the proton on the imine carbon in the product.

Table S1. Crystallographic data and refinement parameters of **SIM-300**.

Compound	**SIM-300**
Formula	$C_{61}H_{48}N_4O_6$
CCDC	2512929
Fw	933.03
Crystal size (mm^3)	0.13 × 0.12 × 0.1
Crystal system	tetragonal
Space group	*I4₁/a*
a (Å)	25.771(2)
b (Å)	25.771(2)
c (Å)	7.6244(5)
α, β, γ (°)	90
V ($Å^3$)	5063.8(10)
Z	4
Radiation	Ga *Kα* (λ = 1.34139)
Data/restraints/parameters	2494/568/292
2θ range (°)	5.968 to 112.172
μ (mm^{-1})	0.404
Reflections collected	11031
R_{int}	0.0626
R_1, wR_2 [I ≥ 2σ (I)]	0.0624, 0.1961
R_1, wR_2 [all data]	0.1375, 0.2512
GOOF	0.954

$R_1 = \Sigma\,(|F_0|-|F_C|)\,/\,\Sigma\,|F_0|$; $wR_2 = [\Sigma\, w\,(|F_0|-|F_C|)^2\,/\,\Sigma\, w\, F_0^2]^{1/2}$

Table S2 Selected bond lengths (Å) for **SIM-300**.

C1−C2	1.551(4)	C11−C12	1.378(11)
C1−C2[1]	1.552(4)	C12−C13	1.366(10)
C1−C2[2]	1.552(4)	C12−C15	1.489(7)
C1−C2[3]	1.552(4)	C13−C14	1.380(8)
C1−C2A[1]	1.563(6)	O1A−C15A	1.227(10)
C1−C2A[3]	1.563(6)	N1A−C5A	1.415(7)
C1−C2A	1.563(6)	N1A−C8A	1.242(8)
C1−C2A[2]	1.563(6)	C2A−C3A	1.411(15)
O1−C15	1.228(7)	C2A−C7A	1.364(13)
N1−C5	1.411(5)	C3A−C4A	1.390(12)
N1−C8	1.244(5)	C4A−C5A	1.413(14)
C2−C3	1.417(9)	C5A−C6A	1.347(12)
C2−C7	1.354(9)	C6A−C7A	1.366(12)
C3−C4	1.373(8)	C8A−C9A	1.468(8)
C4−C5	1.410(10)	C9A−C10A	1.376(9)
C5−C6	1.343(9)	C9A−C14A	1.364(10)
C6−C7	1.376(8)	C10A−C11A	1.376(11)
C8−C9	1.472(6)	C11A−C12A	1.377(15)
C9−C10	1.372(6)	C12A−C13A	1.365(14)
C9−C14	1.367(7)	C12A−C15A	1.490(8)
C10−C11	1.375(8)	C13A−C14A	1.383(11)

[1]5/4-Y, 1/4+X, 5/4-Z; [2]-1/4+Y, 5/4-X, 5/4-Z; [3]1-X, 3/2-Y, +Z

Table S3 Hydrogen bond geometries for the oligomer of **SIM-300**.

D-H	d_{D-H} **(Å)**	$d_{H..A}$ **(Å)**	$\angle_{DHA}$ (°)	$d_{D..A}$ **(Å)**	**A**
C6^a–H6^a	0.930	2.611	127.05	3.257	O1^a

Table S4 Selected bond angles (°) for **SIM-300**.

C2–C1–C2^{1}	109.8(6)	N1–C8–C9	121.9(4)
C2^{1}–C1–C2^{2}	108.8(11)	C10–C9–C8	119.9(5)
C2–C1–C2^{2}	109.8(6)	C14–C9–C8	121.1(4)
C2^{1}–C1–C2^{3}	109.8(6)	C14–C9–C10	118.9(5)
C2–C1–C2^{3}	108.8(11)	C9–C10–C11	120.7(6)
C2^{2}–C1–C2^{3}	109.8(6)	C10–C11–C12	120.4(5)
C2–C1–C2A^{1}	108.4(16)	C11–C12–C15	122.1(7)
C2^{1}–C1–C2A^{2}	102.8(7)	C13–C12–C11	118.6(4)
C2^{1}–C1–C2A^{3}	108.4(16)	C13–C12–C15	119.3(8)
C2^{1}–C1–C2A^{1}	7.7(11)	C12–C13–C14	120.9(6)
C2^{3}–C1–C2A^{3}	7.7(11)	C9–C14–C13	120.4(5)
C2^{2}–C1–C2A^{2}	7.7(11)	O1–C15–C12	122.3(7)
C2^{2}–C1–C2A^{3}	117.0(12)	C8A–N1A–C5A	122.3(8)
C2^{3}–C1–C2A^{2}	108.4(16)	C3A–C2A–C1	118.1(12)
C2^{2}–C1–C2A^{1}	102.8(7)	C7A–C2A–C1	123.3(12)
C2–C1–C2A^{2}	117.0(12)	C7A–C2A–C3A	116.6(7)
C2^{3}–C1–C2A^{1}	117.0(12)	C4A C3A–C2A	120.1(11)
C2–C1–C2A^{3}	102.8(7)	C3A–C4A–C5A	120.5(10)
C2A^{1}–C1–C2A^{2}	97(3)	C4A–C5A–N1A	125.0(11)
C2A^{1}–C1–C2A	116.0(15)	C6A–C5A–N1A	116.9(9)
C2A^{2}–C1–C2A^{3}	116.0(15)	C6A–C5A–C4A	116.9(5)
C2A^{3}–C1–C2A	97(3)	C5A–C6A–C7A	122.9(10)
C2A^{2}–C1–C2A	116.0(15)	C2A–C7A–C6A	121.8(10)
C2A^{1}–C1–C2A^{3}	116.0(15)	N1A–C8A–C9A	122.6(7)
C8–N1–C5	120.8(5)	C10A–C9A–C8A	120.0(7)
C3–C2–C1	116.1(6)	C14A–C9A–C8A	121.4(6)
C7–C2–C1	126.4(6)	C14A–C9A–C10A	118.7(7)
C7–C2–C3	117.5(3)	C11A–C10A–C9A	120.5(8)
C4–C3–C2	120.2(6)	C10A–C11A–C12A	120.6(8)

C3–C4–C5	120.4(6)	C11A–C12A–C15A	121.9(11)
C4–C5–N1	124.9(6)	C13A–C12A–C11A	118.9(6)
C6–C5–N1	117.0(6)	C13A–C12A–C15A	119.2(11)
C6–C5–C4	117.9(3)	C12A–C13A–C14A	120.3(9)
C5–C6–C7	122.0(6)	C9A–C14A–C13A	121.1(8)
C2–C7–C6	121.8(6)	O1A–C15A–C12A	122.1(10)

[1]5/4-Y, 1/4+X, 5/4-Z; [2]-1/4+Y, 5/4-X, 5/4-Z; [3]1-X, 3/2-Y, +Z