Supporting Information for

Guest Removal from Ring-Banded Guanidinium Organosulfonate Hydrogen-Bonded Frameworks

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Video S1. Brightfield video of a $(G)_2(1,5\text{-NDS})\supset EtOH$ single crystal undergoing a transition upon heating at 130°C.

Video S2. Frame-by-frame optical micrographs of the recrystallization process upon heating a $(G)_2(1,5\text{-NDS})\supset EtOH$ banded spherulite film between crossed polarizers. Time-lapse videos of optical micrographs were created in Fiji and frames were stabilized with the StackReg macro plugin.

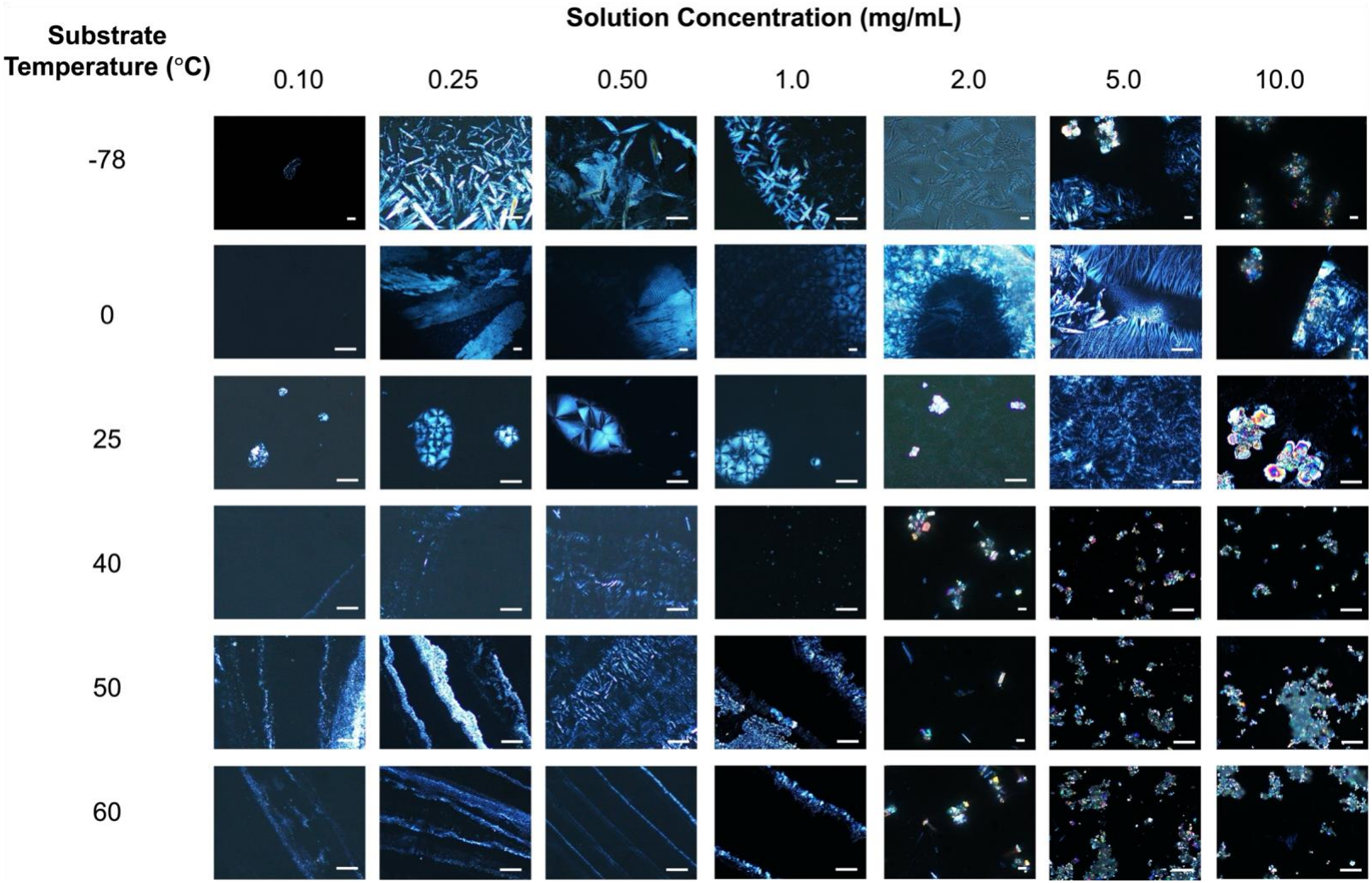


Figure S1. Optical micrographs of $(G)_2$(1,5-NDS) films grown from ethanol solution between crossed polarizers at various solution concentrations and substrate temperatures. Scale bar = 50 μm.

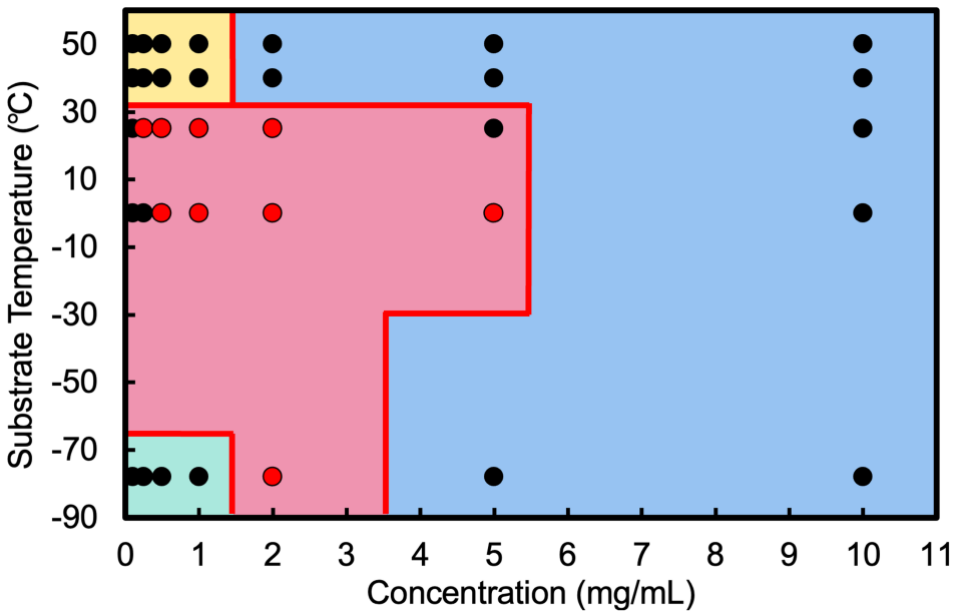


Figure S2. Color map correlating solution concentration and substrate temperature with $(G)_2$(1,5-NDS) film morphologies: (a) coffee rings of small crystalline aggregates (yellow), (b) spherulites (red), (c) needle-like crystals (green), and (d) large crystalline aggregates (blue). Red data points represent banded spherulites.

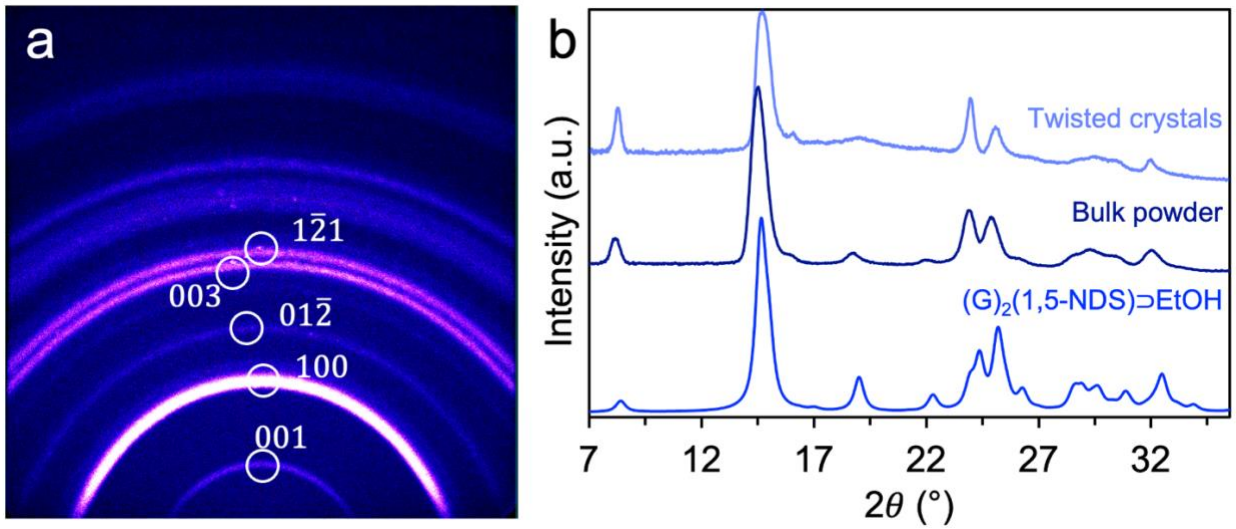


Figure S3. (a) 2-D XRD pattern of $(G)_2$(1,5-NDS)⊃EtOH bulk powder. (b) 1-D line scans extracted from the 2-D diffraction patterns for $(G)_2$(1,5-NDS)⊃EtOH twisted crystals and $(G)_2$(1,5-NDS)⊃EtOH bulk powder loaded into Kapton capillary tubes. The simulated powder XRD pattern of experimentally determined $(G)_2$(1,5-NDS)⊃EtOH are provided for comparison.

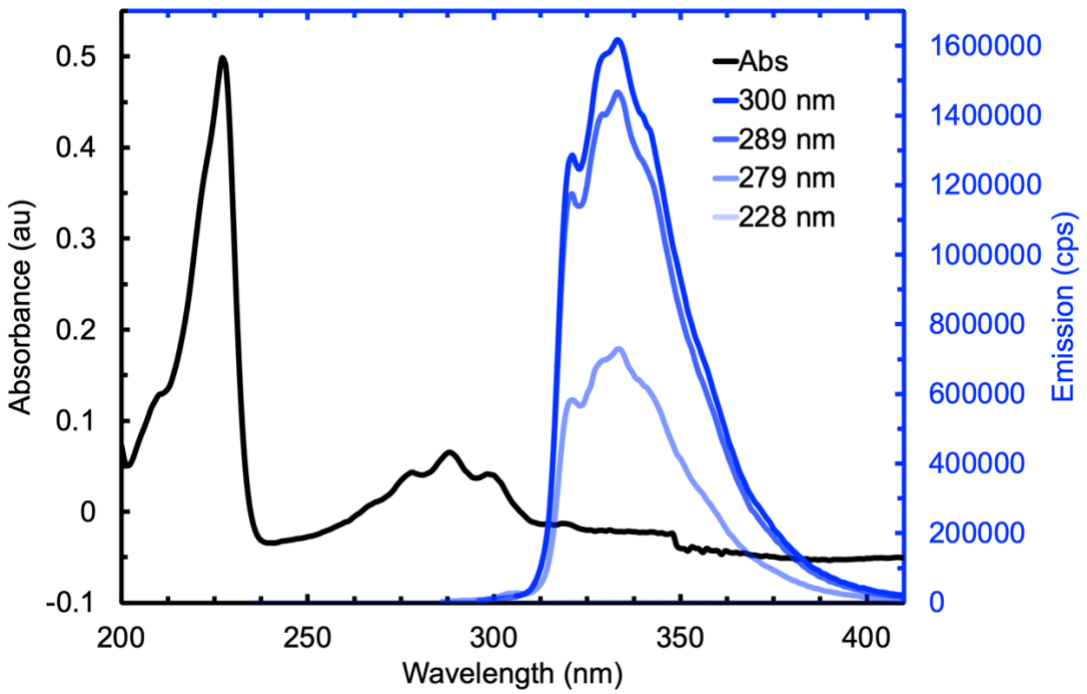


Figure S4. Absorbance and emission spectra at different excitation wavelengths for $(G)_2$(1,5-NDS) dissolved in ethanol.

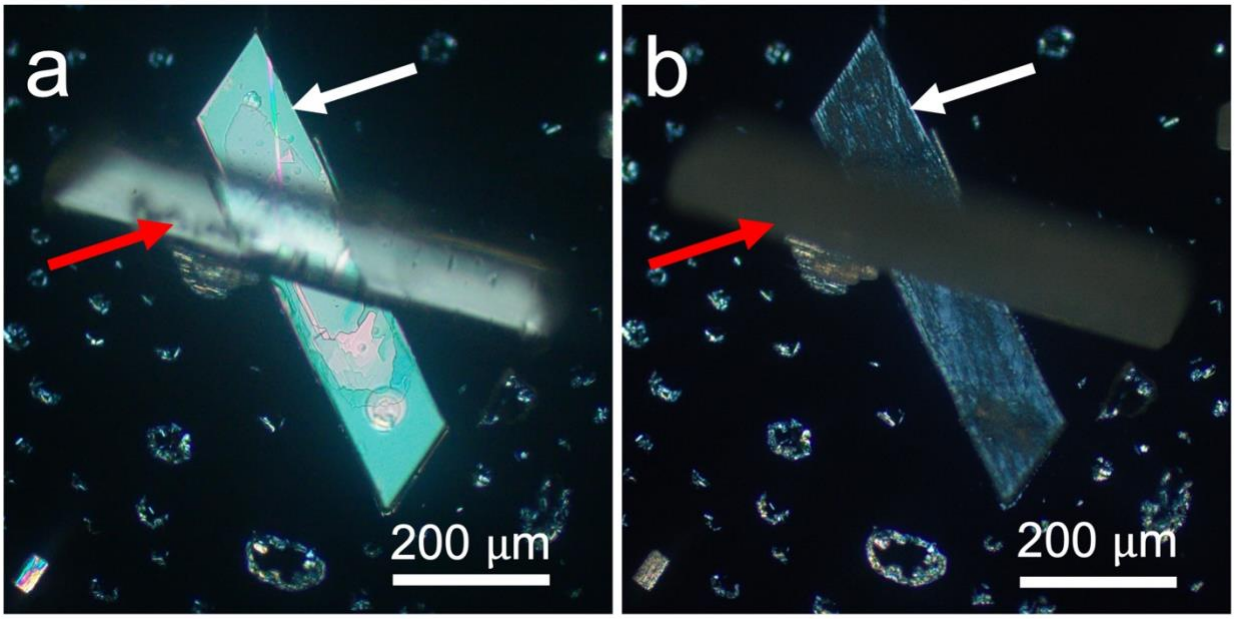


Figure S5. (a, b) Optical micrographs of a $(G)_2$(1,5-NDS)⊃EtOH single crystal between crossed polarizers before and after ethanol guest removal at 130°C, respectively. The white arrow highlights a thin single crystal exhibiting few domains that transformed with loss of retardance. The red arrow indicates a thick single crystal exhibiting multiple domains that decomposed, became dark because of strong scattering, and lost all phase information upon guest removal.

Table S1. Detailed crystallographic data for $(G)_2$(1,5-NDS)⊃EtOH and $(G)_2$(1,5-NDS) collected at 100 K

Compound name	$(G)_2$(1,5-NDS)⊃EtOH	$(G)_2$(1,5-NDS)
Lab code	23mdw12ay	23mdw35ay
CCDC no.	2419508	-
Formula by X-ray	$C_{14}H_{24}N_6O_7S_2$	$C_{12}H_{18}N_6O_6S_2$
Formula weight	452.51	406.44
Crystal habit	colorless plate	cloudy colorless prism
Crystal size (mm)	0.430 x 0.370 x 0.110	0.886 x 0.471 x 0.190
Crystal system	triclinic	monoclinic
Space group (no.)	$P\bar{1}$	$P2_1/c$
a **(Å)**	7.2940(3)	11.359(5)
b **(Å)**	7.2975(3)	9.285(4)
c **(Å)**	11.5957(5)	9.048(4)
α **(°)**	100.0921(15)	90
β **(°)**	95.3125(14)	101.453(12)
γ **(°)**	118.9930(13)	90
V **(Å³)**	520.096	935.276
Z	1	2
D_c **(g cm^{-3})**	1.445	1.443
F**(000)**	238.0	424.0
μ (mm^{-1})	0.305	0.326
Total reflections	15215	2443
Unique reflections	2576	640
R_{int}	0.0327	0.0953
R_1 **[*I*>2σ(*I*)]**	0.0325	0.1106
wR_2 **(all data)**	0.0946	0.2229
GOF (all data)	1.085	1.386

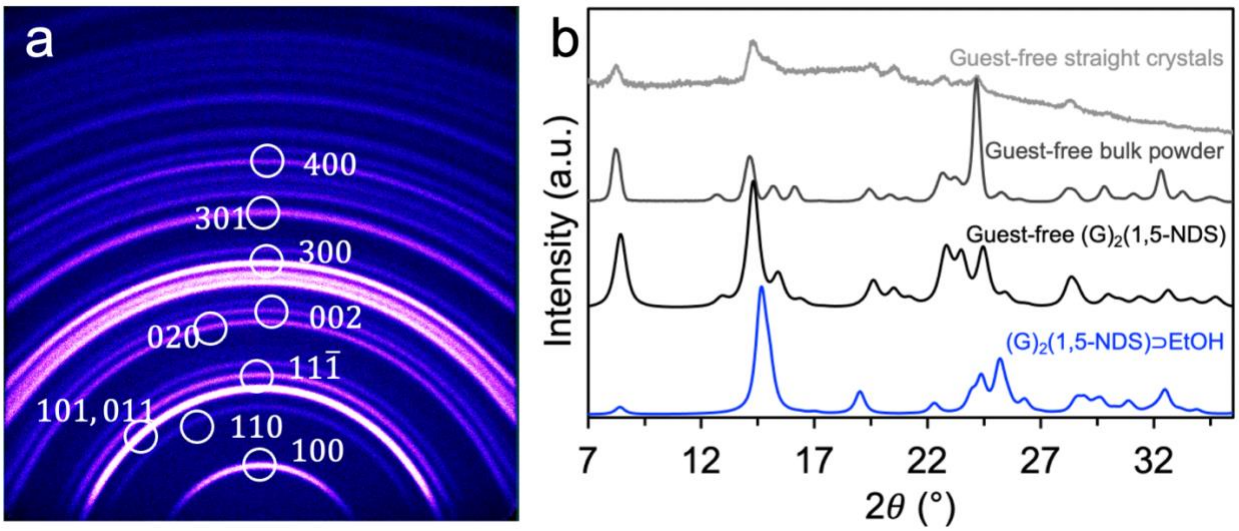


Figure S6. (a) 2-D XRD pattern of guest-free $(G)_2$(1,5-NDS) bulk powder. (b) 1-D line scans extracted from the 2-D diffraction patterns of guest-free $(G)_2$(1,5-NDS) straight crystals and guest-free $(G)_2$(1,5-NDS) bulk powder loaded into Kapton capillary tubes. The simulated powder XRD patterns of experimentally determined guest-free $(G)_2$(1,5-NDS) and $(G)_2$(1,5-NDS)⊃EtOH are provided for comparison.

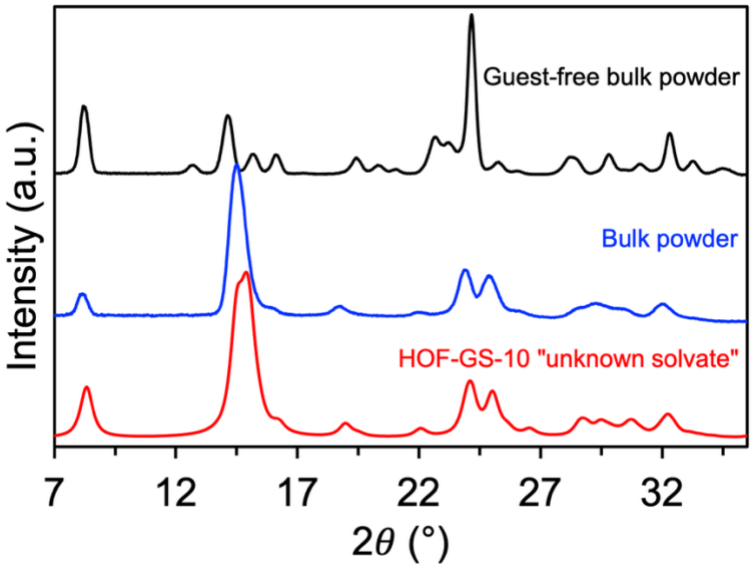


Figure S7. Comparison of 1-D line scans extracted from the 2-D diffraction patterns of $(G)_2$(1,5-NDS)⊃EtOH bulk powder and guest-free $(G)_2$(1,5-NDS) bulk powder with the simulated powder XRD pattern of experimentally determined HOF-GS-10 "unknown solvate".

Table S2. Comparison of crystallographic data for $(G)_2$(1,5-NDS)⊃EtOH, $(G)_2$(1,5-NDS) and HOF-GS-10.

Compound name	**$(G)_2$(1,5-NDS)⊃EtOH**	**$(G)_2$(1,5-NDS)**	**HOF-GS-10**
CCDC no.	2419508	-	1473368
Formula by X-ray	$C_{14}H_{24}N_6O_7S_2$	$C_{12}H_{18}N_6O_6S_2$	$C_{12}H_{18}N_6O_6S_2$
Formula weight	452.51	406.44	406.44
Crystal habit	colorless plate	cloudy colorless prism	colorless rod
Crystal size (mm)	0.430 x 0.370 x 0.110	0.886 x 0.471 x 0.190	0.13 x 0.11 x 0.10
Crystal system	triclinic	monoclinic	triclinic
Space group (no.)	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a **(Å)**	7.2940(3)	11.359(5)	7.2631(10)
b **(Å)**	7.2975(3)	9.285(4)	7.3084(11)
c **(Å)**	11.5957(5)	9.048(4)	11.6934(17)
α **(°)**	100.0921(15)	90	74.902(4)
β **(°)**	95.3125(14)	101.453(12)	84.809(4)
γ **(°)**	118.9930(13)	90	60.567(4)
V **(Å^3)**	520.096	935.276	521.41(13)
Z	1	2	1
D_c **(g cm^{-3})**	1.445	1.443	1.294

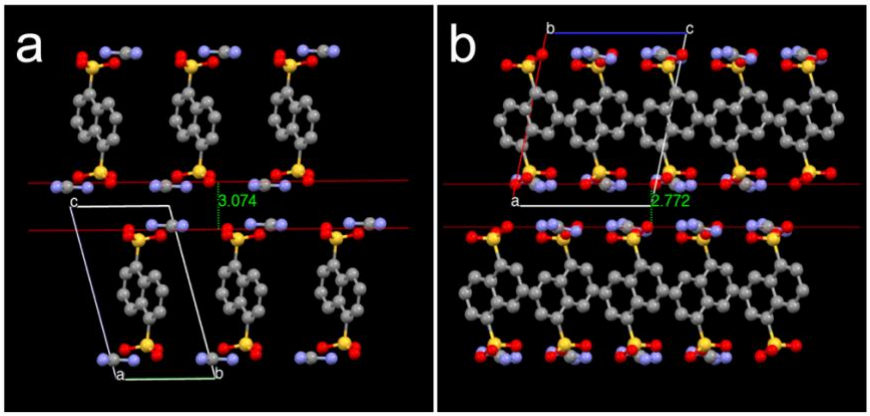


Figure S8. Molecular packing highlighting the distance between adjacent bilayers in (a) $(G)_2$(1,5-NDS)⊃EtOH and (b) $(G)_2$(1,5-NDS) as 3.074 Å and 2.772 Å, respectively, as measured by the distance between a plane constructed through the closest oxygen atoms in each bilayer. Hydrogen atoms are hidden for clarity.

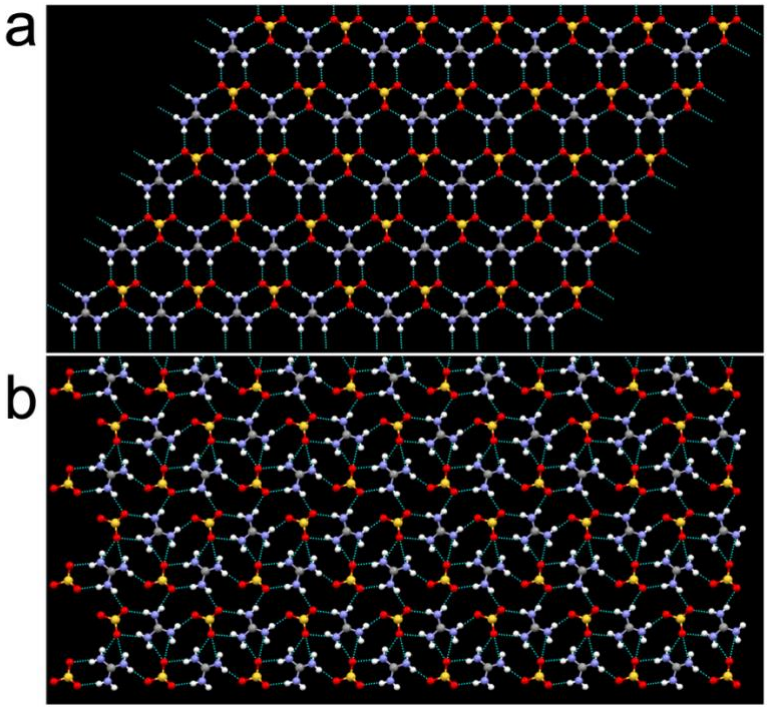


Figure S9. (a, b) Hydrogen-bonding interactions in GS sheets of $(G)_2$(1,5-NDS)⊃EtOH and $(G)_2$(1,5-NDS). Unlike $(G)_2$(1,5-NDS)⊃EtOH, $(G)_2$(1,5-NDS) exhibits a distorted quasi-hexagonal GS sheet. In $(G)_2$(1,5-NDS), G cations and S anions retain the 6 strong hydrogen bonds (d(N--O) = 2.869, 2.889, 2.929, 2.952, 2.968, 3.038 Å), albeit the magnitudes of these hydrogen bonding interactions differ slightly in $(G)_2$(1,5-NDS)⊃EtOH (d(N--O) = 2.900, 2.912, 2.927, 2.927, 2.937, 2.948 Å). One pair of G protons on adjacent nitrogen atoms is hydrogen-bonded to a single S oxygen atom. While $(G)_2$(1,5-NDS)⊃EtOH has each G cation bound to only 3 S anions, each G cation is bound to 4 S anions in $(G)_2$(1,5-NDS). Hydrogen bonds in $(G)_2$(1,5-NDS) are slightly longer on average (2.941 *vs.* 2.925 Å) than in the $(G)_2$(1,5-NDS)⊃EtOH structure, and their geometry appears to be much less favorable: N-H--O angles in $(G)_2$(1,5-NDS) are 167.25°, 145.57°, 147.47°, 145.70°, 156.86°, and 161.66°, compared to N-H--O angles of 163.11°, 165.15°, 174.47°, 160.58°, 159.45°, and 170.42° in the $(G)_2$(1,5-NDS)⊃EtOH structure.

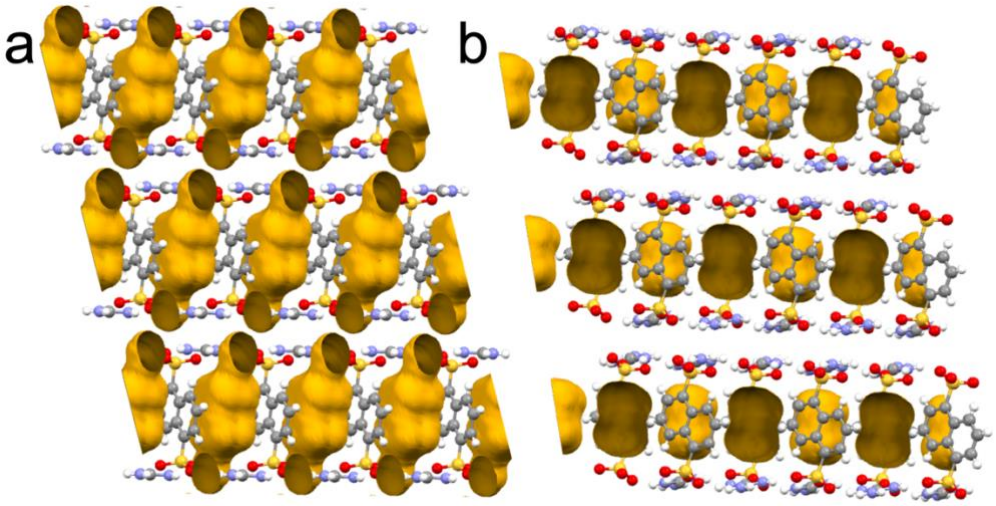


Figure S10. Visualization of the calculated void spaces (yellow cavities) in (a) $(G)_2$(1,5-NDS)⊃EtOH with ethanol computationally removed compared to (b) $(G)_2$(1,5-NDS). The voids are 19.6% and 9.7% of the unit cell volume, affording void volumes of 101.95 $Å^3$ and 90.82 $Å^3$, respectively (grid spacing = 0.3 Å, probe radius = 1.2 Å).

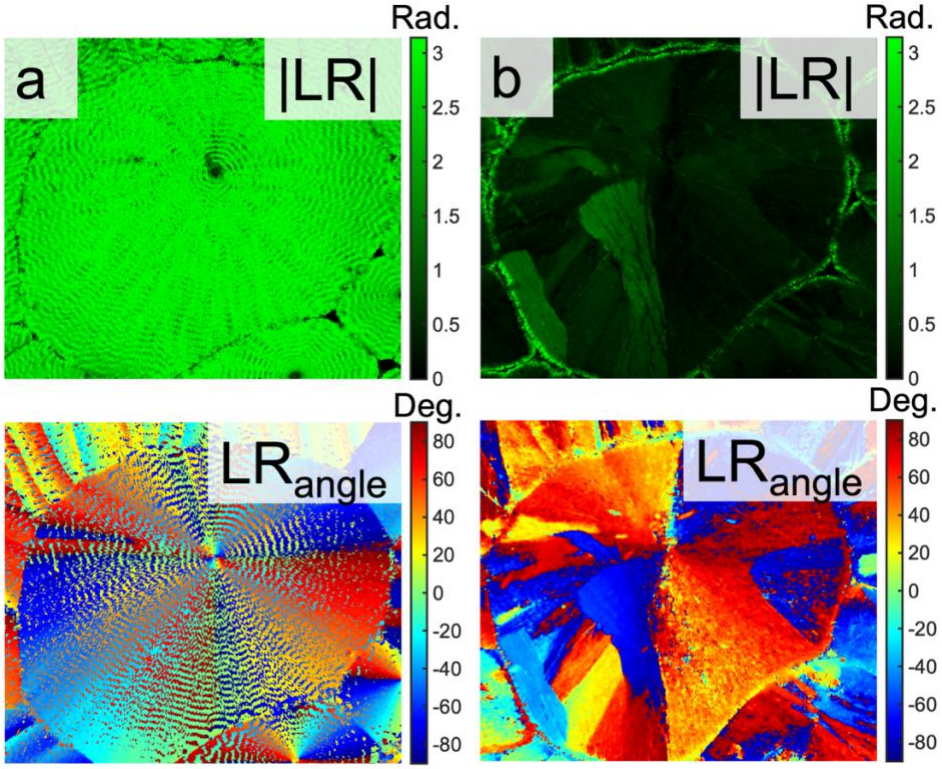
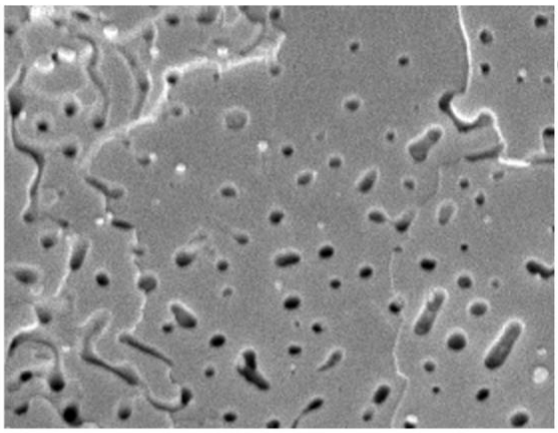
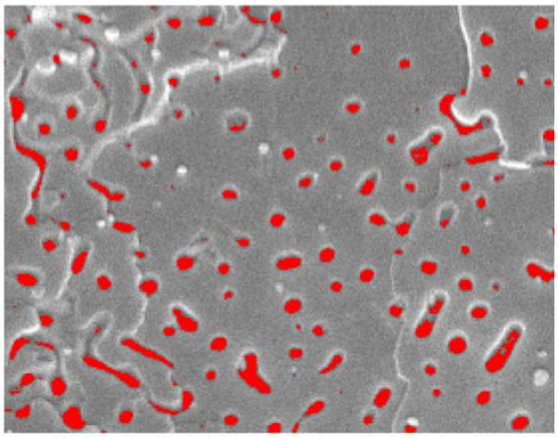


Figure S11. Linear retardance (|LR|) map and angle-dependent linear retardance (LR_{angle}) map measured in degrees counterclockwise from the horizontal direction (a) before and (b) after guest removal from $(G)_2$(1,5-NDS)⊃EtOH banded spherulite films. λ = 455 nm.

a



b



c

Pore Parameter	Value
Count[1]	142
Total Area[2]	0.908
Average Size[3]	0.006
%Area[4]	5.557
Perimeter[5]	0.29
Circularity[6]	0.861
Solidity[7]	0.855
Feret[8]	0.122
FeretX[9]	121.746
FeretY[10]	106.211
FeretAngle[11]	101.988
MinFeret[12]	0.069

[1]Number of pores detected; [2]Sum of all pore areas (in μm²); [3]Mean pore area (in μm²); [4]Percentage of the image area occupied by pores; [5]Combined boundary length of each pore (in μm); [6]4π × (Area) / (Perimeter²), ranges 0–1 (1 = perfect circle); [7]Ratio of pore area to its convex hull area (1 = fully convex); [8]Maximum caliper diameter (longest chord, in μm); [9]Coordinates of the Feret diameter start point; [10]Angle (in degrees) of the Feret diameter relative to the x-axis; [11]Minimum caliper diameter (shortest chord, in μm)

Figure S12. (a) SEM cross-section of a guest-free $(G)_2$(1,5-NDS) film, (b) cross-section of the film with pores shaded in red, and (c) tabular summary of measurements obtained from pore analysis conducted using Fiji software.