Guest Exchange through Single Crystal-Single Crystal Transformations in a Flexible Hydrogen-Bonded Framework

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Supporting information

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Table S2. Crystallographic information for crystals A, B and C mentioned in Figure S10.

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Figure S14. (A) Crystal of $G_4TSPB^-(dioxane)_5$ and indexed faces. (B) Crystal from A after immersion in toluene for four hours, transforming to $G_4TSPB^-(toluene)_3(dioxane)$. (C) Crystal from B after immersion in dioxane for four hours, reverting back to $G_4TSPB^-(dioxane)_5$.

Table S3. Crystallographic information for crystals A, B and C in Figure S14.

Figure S15. Powder X-ray diffraction illustrating the reversibility of transformation between $G_4TSPB^-(dioxane)_5$ and $G_4TSPB^-(toluene)_3(dioxane)$. From bottom to top: (black) Powder pattern calculated from the single crystal structure of $G_4TSPB^-(dioxane)_5$; (red) $G_4TSPB^-(dioxane)_5$ after immersion in toluene for four hours followed by immersion in dioxane for four hours; (blue) first repetition of the same cycle; (green) second repetition of the same cycle; (purple) third repetition of the same cycle; (brown) fourth repetition of the same cycle.

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Table S4. Crystallographic information for crystals A, B and C in Figure S19.

Figure S20. From bottom to top: (black) NMR spectrum of a $G_4TSPB^-(THF)_5$ single crystal; (red) $G_4TSPB^-(THF)_5$ single crystal after immersion in toluene for four hours, transforming to $G_4TSPB^-(toluene)_3(THF)_{0.5}$; (blue) $G_4TSPB^-(toluene)_3(THF)_{0.5}$ single crystal after immersion in THF for four hours, reverting to $G_4TSPB^-(THF)_5$. NMR solvent: dimethylsulfoxide.

Figure S21. (black curve) TGA of $G_4TSPB^-(THF)_5$; (red curve) $G_4TSPB^-(toluene)_3(THF)_{0.5}$. Heating rate = 10 ^oC/min.

Figure S22. Powder X-ray diffraction illustrating the reversibility of transformation between $G_4TSPB^-(THF)_5$ and $G_4TSPB^-(toluene)_3(THF)_{0.5}$. From bottom to top: (black) Powder pattern calculated from the single crystal structure of $G_4TSPB^-(THF)_5$; (red) $G_4TSPB^-(THF)_5$ after immersion in toluene for four hours followed by immersion in THF for four hours; (blue) first repetition of the same cycle; (green) second repetition of the same cycle; (purple) third repetition of the same cycle; (brown) fourth repetition of the same cycle.

Figure S23. (A) Crystal of $G_4TSPB^-(toluene)_3(dioxane)$ and indexed faces. (B) Crystal from A after immersion in THF for four hours, transforming to $G_4TSPB^-(THF)_5$.

Table S5. Crystallographic information for crystals A and B in Figure S23.

Figure S24. From bottom to top: (black) NMR spectrum of a $G_4TSPB^-(toluene)_3(dioxane)$ single crystal; (red) $G_4TSPB^-(toluene)_3(dioxane)$ single crystal after immersion in THF for four hours, transforming to $G_4TSPB^-(THF)_5$. NMR solvent: dimethylsulfoxide.

Figure S25. (A) Crystal of $G_4TSPB^{\cdot}(toluene)_3(THF)_{0.5}$ and indexed faces. (B) Crystal from A after immersion in dioxane for four hours, transforming to $G_4TSPB^{\cdot}(dioxane)_5$.

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Figure S26. From bottom to top: (black) NMR spectrum of a $G_4TSPB^{\cdot}(toluene)_3(THF)_{0.5}$ single crystal; (red) $G_4TSPB^{\cdot}(toluene)_3(THF)_{0.5}$ single crystal after immersion in dioxane for four hours, transforming to $G_4TSPB^{\cdot}(dioxane)_5$. NMR solvent: dimethylsulfoxide.

Figure S27. From bottom to top: (black) NMR spectrum of G_4TSPB precipitate formed by layering toluene on a methanol solution of G_4TSPB; (red) G_4TSPB precipitate formed by layering a methanol solution of G_4TSPB on aniline; (orange) G_4TSPB precipitate formed by layering a methanol solution of G_4TSPB on nitrobenzene. NMR solvent: dimethylsulfoxide.Attempts to grow single crystals of toluene, aniline and nitrobenzene inclusion compounds were not successful.

Figure S28. (black) Powder X-ray diffraction characterization of G_4TSPB precipitate formed by layering toluene on a methanol solution of G_4TSPB; (red) G_4TSPB precipitate formed by layering a methanol solution of G_4TSPB on aniline; (blue) G_4TSPB precipitate formed by layering a methanol solution of G_4TSPB on nitrobenzene.

Materials and general procedures

All chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received.

Synthesis of guanidinium 1,2,4,5-tetra(4-sulfonatophenyl)-benzene (G$_4$TSPB). 2 g 1,2,4,5-tetrabromo-benzene, 3.66 g phenylboronic acid, 0.3 g Tetrakis(triphenylphosphine)palladium and 8.3 g K_2CO_3 were suspended in a solution comprising 30 mL ethanol, 30 mL water, and 60 mL toluene. The mixture was heated at 95 ^oC for 18 hours. After cooling to room temperature, 300 mL of toluene was added and the mixture was stirred for one hour. The organic layer was washed with 1M NaOH twice and then dried with anhydrous $MgSO_4$. Excess toluene was removed by rotary evaporator, and the solid product was re-crystallized in hexane to afford 1.2 g of an off-white solid (1,2,4,5-tetraphenylbenzene, Yield = 62% based on 1,2,4,5-tetrabromo-benzene). The solid was then heated under reflux in 6 mL of 95% H_2SO_4 for 18 hours, after which the hot solution was poured into 100 mL of deionized water. NaOH was added to adjust the pH to pH = 14, and then 1.7 g N(butyl)$_4$Cl was added. The mixture was then extracted with CH_2Cl_2, the organic layer dried with anhydrous $MgSO_4$, and excess solvent removed. The resulting solid was then passed through a column packed with Amberlyst 36 ion exchange resin. To the eluent was added 2 g of guanidinium tetrafluoroborate. The mixture was then dried with a rotary evaporator, and the resulting solid mixture was washed with hot acetone several times and dried by allowing standing in air at room temperature, affording 1.7 g of off-white **G$_4$TSPB**. ^{1}H NMR (400M, DMSO): 7.50 (d, 8H), 7.43 (s, 2H), 7.19 (d, 8H), 6.94 (s, 24H). Elemental analysis for $C_{34}H_{46}O_{12}S_4N_{12}$. Calculated: C (43.28%), H (4.88%), N (17.82%); measured: C (43.55%), H (5.03%), N (18.35%). IR: 3417 (w), 3195 (w), 1667 (s), 1179 (w), 1127 (s), 1035 (s), 1008 (s), 1000 (s), 832 (s), 753 (s), 691 (m), 661 (s).

Preparation of G$_4$TSPB$^-$(dioxane)$_5$. 20 mg G$_4$TSPB was dissolved in 0.4 mL water, followed by diffusion of dioxane vapor into the solution, affording single crystals. Elemental analysis for $C_{54}H_{86}O_{22}S_4N_{12}$. Calculated: C (46.89%), H (6.22%), N (12.17%); measured: C (47.31%), H (6.38%), N (12.05%). IR: 3368 (w), 3194 (w), 1663 (s), 1596 (w), 1475 (m), 1187 (w), 1121 (s), 1036 (s), 1000 (m), 873 (s), 830 (s), 755 (s), 660 (m).

Preparation of G$_4$TSPB$^-$(dioxane)$_4$. Single crystals of G$_4$TSPB$^-$(dioxane)$_5$ were exposed to air under ambient conditions for one day, affording G$_4$TSPB$^-$(dioxane)$_4$. Elemental analysis for $C_{50}H_{78}O_{20}S_4N_{12}$. Calculated: C (46.37%), H (6.03%), N (12.98%); measured: C (46.24%), H (6.11%), N (12.69%). IR: 3367 (w), 3196 (w), 1663 (s), 1596 (w), 1475 (m), 1187 (w), 1121 (s), 1036 (s), 1001 (m), 873 (s), 830 (s), 755 (s), 660 (m).

Preparation of G$_4$TSPB$^-$(tetrahydrofuran)$_5$. Single crystals of G$_4$TSPB$^-$(dioxane)$_5$ were immersed in tetrahydrofuran for four hours, affording G$_4$TSPB$^-$(tetrahydrofuran)$_5$. Elemental Analysis for

$C_{54}H_{86}O_{17}S_4N_{12.}$ Calculated: C (49.77%), H (6.61%), N (12.90%); measured: C (49.62%), H (6.52%), N (13.17%). IR: 3421 (w), 3360 (w), 3174 (s), 1669 (s), 1187 (s), 1128 (s), 1034 (s), 1008 (s), 829 (s), 692 (s), 656 (s), 579 (s), 537 (s).

Preparation of $G_4TSPB^-(toluene)_3(dioxane)$: Single crystals of $G_4TSPB^-(dioxane)_5$ were immersed in toluene for four hours, crystals affording $G_4TSPB^-(toluene)_3(dioxane)$. Elemental Analysis for $C_{59}H_{78}O_{14}S_4N_{12.}$ Calculated: C (54.21%), H (5.97%), N (12.86%); measured: C (53.88%), H (6.03%), N (12.96%). IR: 3419 (w), 3178 (w), 1669 (s), 1187 (s), 1128 (s), 1034 (s), 1008 (s), 828 (s), 692 (s), 659 (s), 579 (s).

Preparation of $G_4TSPB^-(toluene)_3(tetrahydro\text{-}furan)_{0.5}$. Single crystals of $G_4TSPB^-(tetrahydrofuran)_5$ were immersed in toluene for four hours, affording $G_4TSPB^-(toluene)_3(tetra\text{-}hydrofuran)_{0.5}$. Elemental Analysis for $C_{57}H_{74}O_{12.5}S_4N_{12.}$ Calculated: C (54.54%), H (5.90%), N (13.39%); measured: C (54.10%), H (6.03%), N (13.67%). IR: 3421 (w), 3360 (w), 3174 (s), 1669 (s), 1187 (s), 1128 (s), 1034 (s), 1008 (s), 828 (s), 692 (s), 656 (s), 579 (s), 537 (s).

Characterization. Infrared spectra were collected with a Magna-IR spectrometer 550. NMR data was collected under Bruker AV-400 High Performance Digital NMR Spectrometer (400 MHz). Thermal gravimetric analysis (TGA) was performed with a Perkin Elmer Pyris 1. Elemental analysis was performed with a Perkin Elmer Series II 2400.

X-ray Diffraction Methods

Single Crystal X-ray Diffraction. Data using Mo radiation was collected on a Bruker SMART APEX II diffractometer equipped with a CCD detector and operated at 1,500W power (50KV, 30mA) to generate Mo Kα radiation (λ = 0.71073 Å), which is graphite monochromated and MonoCap-collimated. The crystal was mounted on an 0.3 mm 20-micron-thick Nylon Cryoloop (Hampton Research) with Immersion Oil of Type B (Cargille Labs) frozen at 100 K with an Oxford Cryosystems 700 plus Cooler. Preliminary lattice parameters and orientation matrices were obtained from three sets of frames. Then full data were collected using the ω scan method with the frame width of 0.5[1]. Data were processed with the SAINT+ program[2] for reduction and cell refinement. Multi-scan absorption corrections were applied by using the SADABS program for area detector. All structures were solved by the direct method (SHELXS-97) and refined on F^2 (SHELXL-97)[3] . Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms on carbons were placed in idealized positions (C-H = 0.93 or 0.96 Å) and included as riding with Uiso(H) = 1.2 or 1.5 Ueq(non-H). The PLATON/SQUEEZE[4] procedure was applied to handle the heavily disordered components (ions and solvents) in the voids of the frameworks. Pore size was calculated from Mercury software, using probe radius 1.2 Å. Guest molecule volume was

calculated from Material Studio through following procedures: 1 optimize molecular geometry; 2 generate solvent accessible surface under forcite "ultra fine" model (probe raidus 1.2 Å); 3 calculate molecular volume.

Powder X-Ray Diffraction. Powder X-ray diffraction (PXRD) was performed with a Bruker D8 Discover Microdiffractometer with the General Area Detector Diffraction System (GADDS) equipped with a VÅNTEC-2000 2D detector. The X-ray beam was monochromated with a graphite crystal (λ Cu-Kα = 1.54178 Å) and collimated with a 0.5 mm capillary collimator (MONOCAP). The powder sample was filled in a 0.8 mm capillary tube and mounted in a vertical configuration on a sample stage affixed to a five-circle Eulerian cradle. The two-dimensional (2D) diffraction data was collected by the software GADDS.[5] Two scans (or one scan) with the rotation of the capillary were acquired at the incident angle (θ_1) = detector angle (θ_2) = 10° and 25°, respectively. At each angle, the exposure time was 10 minutes. The sample-to-detector distance was 150 mm. One-dimensional diffraction patterns were generated by integrating the 2D XRD data using XRD2EVAL in the Bruker PILOT software.[6] The integrated 1D pattern was analyzed by the software DIFFRAC^{plus} EVA[5]. The simulated 1D powder pattern was calculated by the software Mercury.[7]

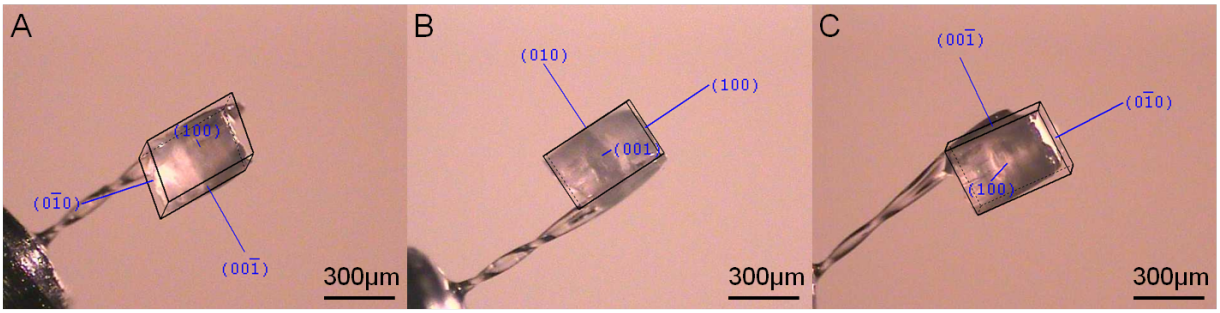

Figure S1. (A) Crystal of $G_4TSPB^-(dioxane)_5$ and indexed faces. (B) Crystal from A after standing in ambient air for one day, transforming to $G_4TSPB^-(dioxane)_4$), and its indexed faces. (C) Crystal from B after immersion in dioxane for four hours, reverting $G_4TSPB^-(dioxane)_5$, and its indexed faces.

Table S1. Crystallographic information for crystals A, B and C in Figure S1.

compound	$G_4TSPB^-(dioxane)_5$	$G_4TSPB^-(dioxane)_4$	$G_4TSPB^-(dioxane)_5$
formula	$C_{54}H_{82}N_{12}O_{22}S_4$	$C_{50}H_{74}N_{12}O_{20}S_4$	$C_{54}H_{82}N_{12}O_{22}S_4$
crystal system	Triclinic	Monoclinic	Triclinic
space group	$P1$	$P2_1$	$P1$
color	Colorless	Colorless	Colorless
a (Å)	16.068(4)	6.001(3)	16.11
b (Å)	18.326(4)	35.559(15)	18.42
c (Å)	35.252(8)	15.223(6)	35.40
α (deg)	80.336(3)	90	80.21
β (deg)	85.481(3)	101.047(4)	85.42
γ (deg)	77.775(3)	90	77.75
V (Å^3)	9990.95	3188.24	10106
temp (K)	100(2)	100(2)	100(2)
Z	6	2	\
R_1 [$I > 2\sigma(I)$]	0.1302	0.1344	\

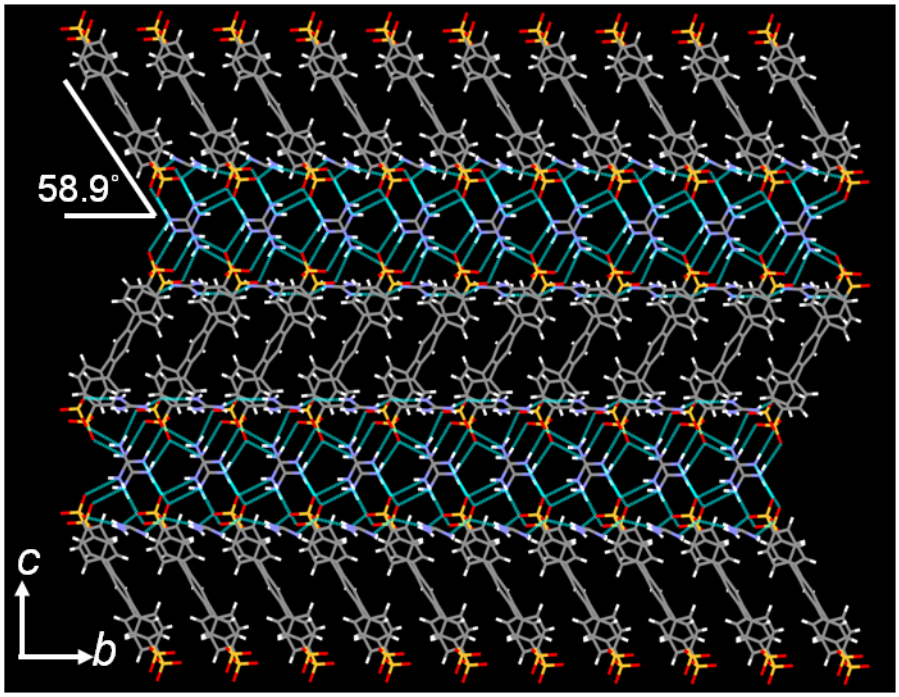

Figure S2. Side view of the G_4TSPB cylinders, which are oriented along the *a* axis. Dioxane molecules are removed for clarity.

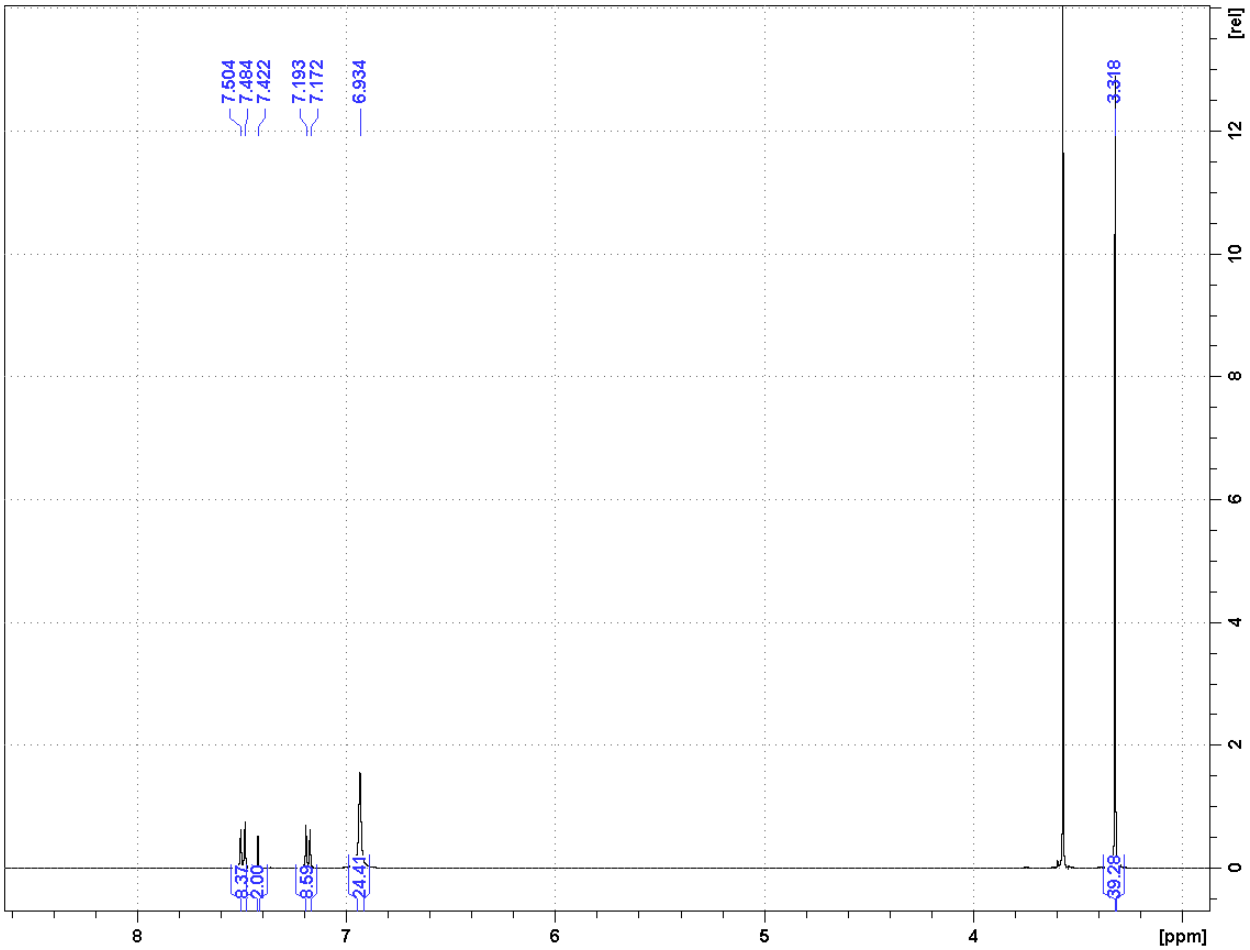

Figure S3. NMR spectrum of a $G_4TSPB^-(dioxane)_5$ single crystal, indicating a host:dioxane ratio of 1:5. NMR solvent: dimethylsulfoxide.

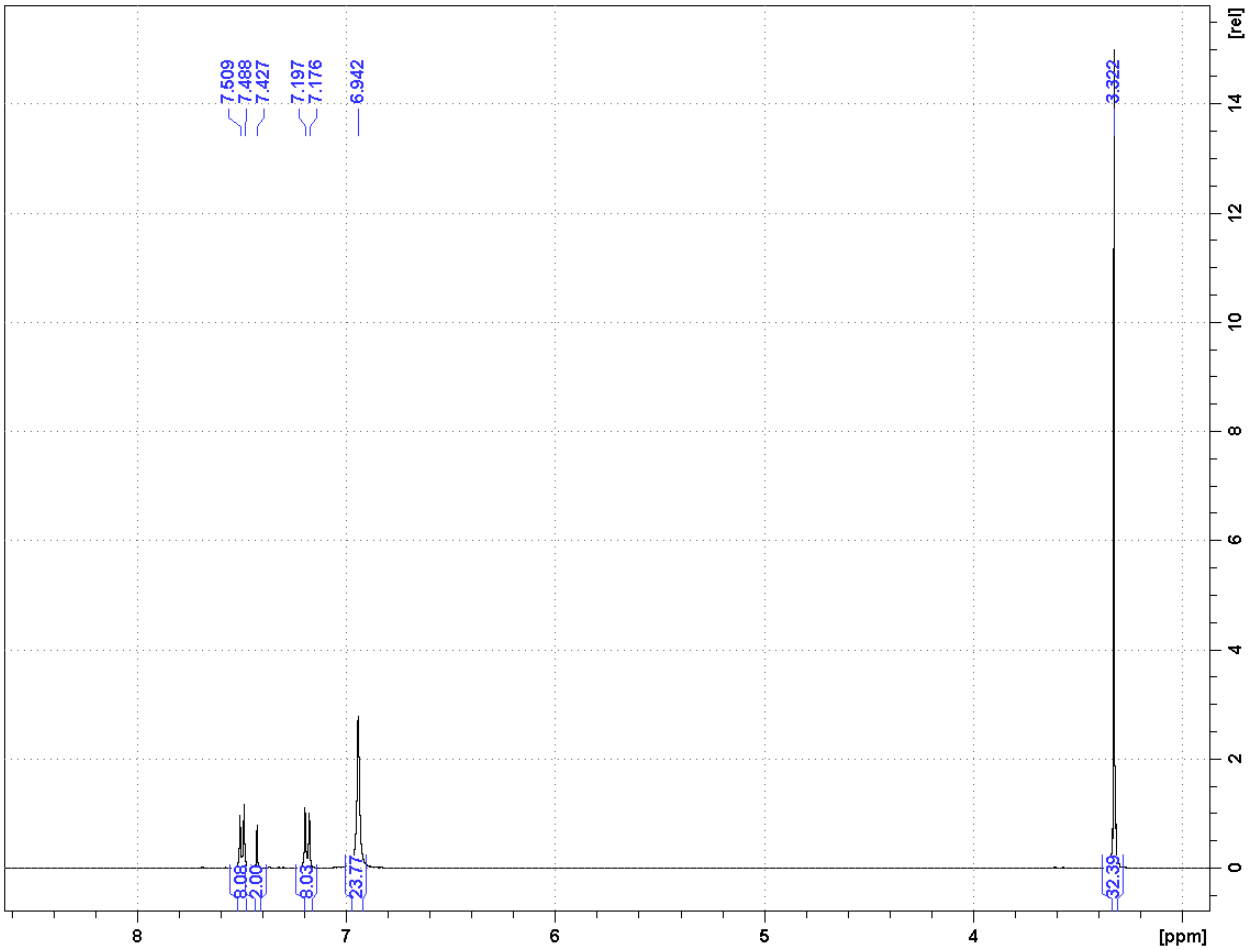

Figure S4. NMR spectrum of a $G_4TSPB^-(dioxane)_4$ single crystal, indicating a host:dioxane ratio of 1:4. NMR solvent: dimethylsulfoxide.

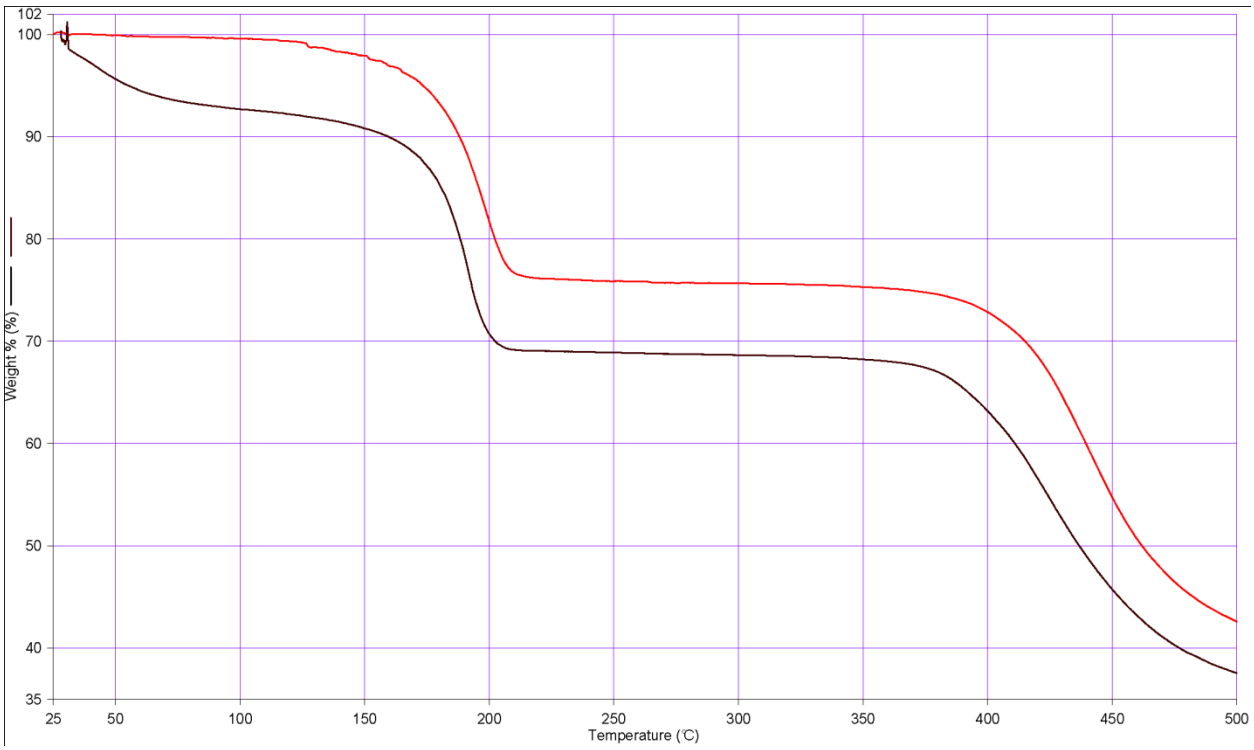

Figure S5. (black curve) TGA of $G_4TSPB^-(dioxane)_5$; (red curve) $G_4TSPB^-(dioxane)_4$. Heating rate = 10 ^oC/min.

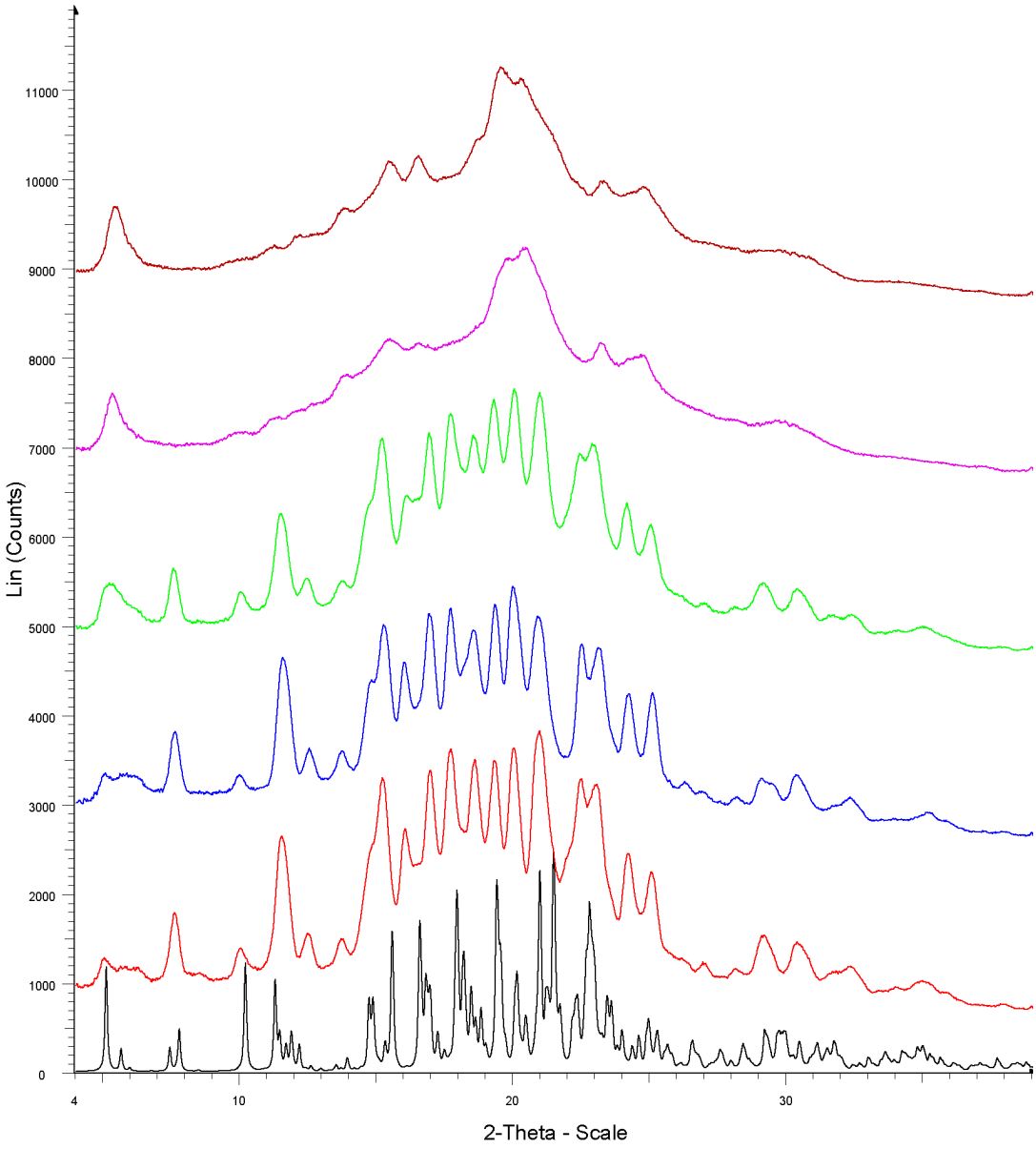

Figure S6. Powder X-ray diffraction illustrating the reversibility of transformation between $G_4TSPB^{\cdot}(dioxane)_5$ and $G_4TSPB^{\cdot}(dioxane)_4$. From bottom to top: (black) Powder pattern calculated from the single crystal structure of $G_4TSPB^{\cdot}(dioxane)_5$; (red) $G_4TSPB^{\cdot}(dioxane)_5$ after standing in air for one day, followed by immersion in dioxane for four hours; (blue) repetition of the same cycle; (green) second repetition of the same cycle; (purple) third repetition of the same cycle; (brown) fourth repetition of the same cycle.

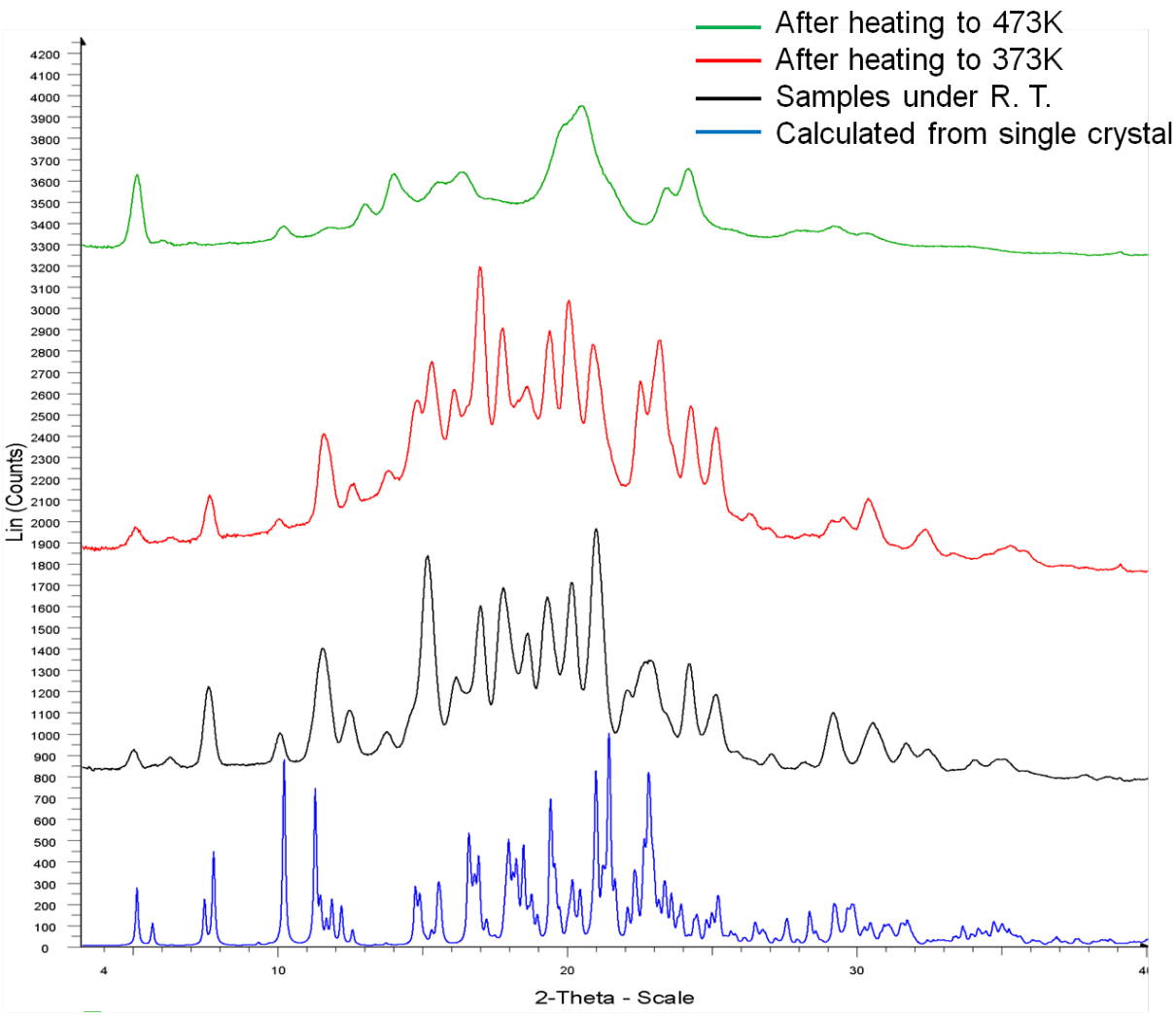

Figure S7. Powder X-ray diffraction characterization of $G_4TSPB^-(dioxane)_5$ upon heating to various temperature. From bottom to top: (blue) Powder diffraction pattern calculated from the single crystal structure of $G_4TSPB^-(dioxane)_5$, (black) $G_4TSPB^-(dioxane)_5$ at room temperature; (red) after heating to 373 K, after heating to 473 K (green).

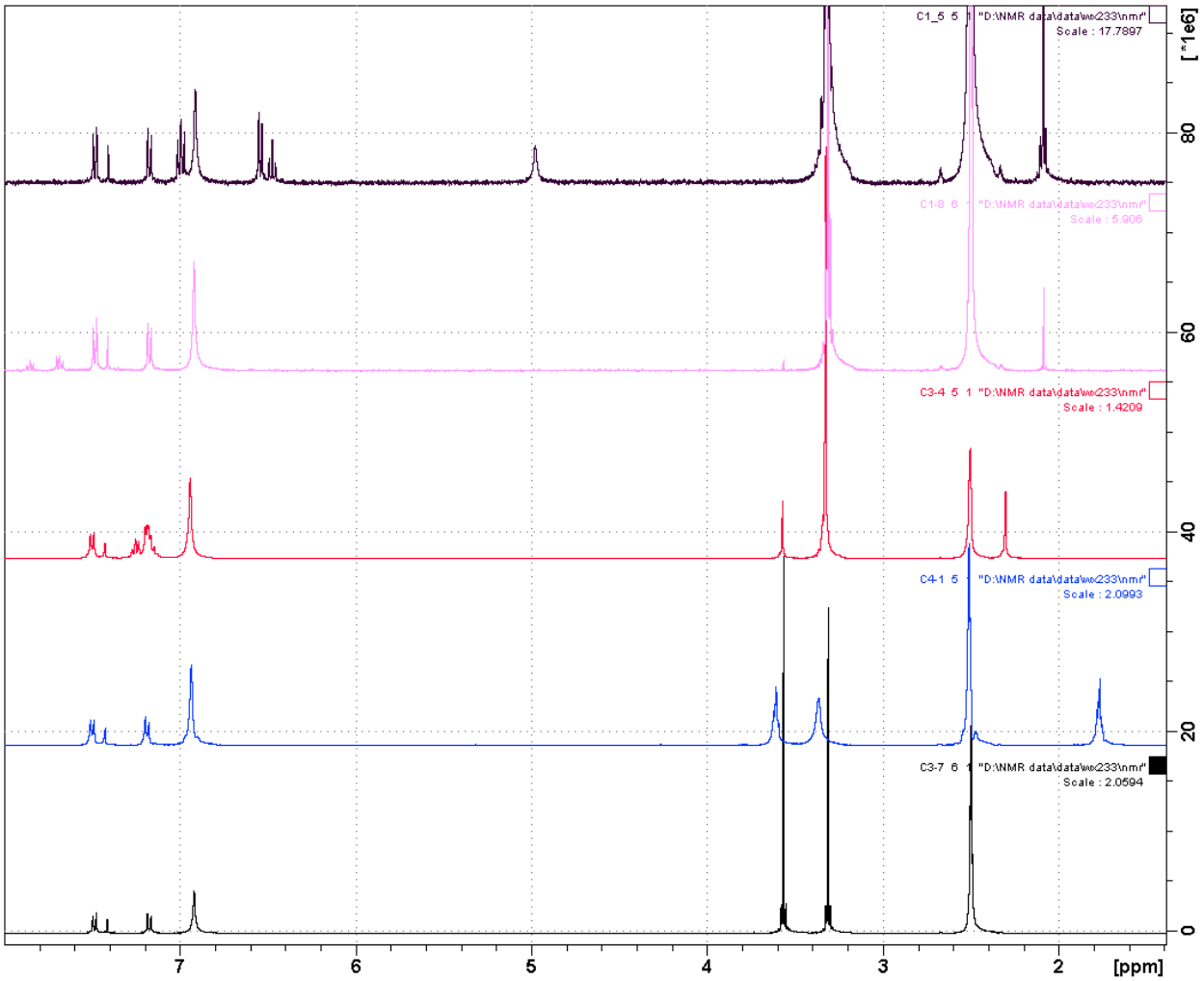

Figure S8. (black at bottom) NMR spectra of a $G_4TSPB^-(dioxane)_5$ single crystal; (blue) $G_4TSPB^-(dioxane)_5$ single crystal after immersion for four hours in THF, transforming to $G_4TSPB^-(THF)_5$; (red) $G_4TSPB^-(dioxane)_5$ single crystal after immersion for four hours in toluene, transforming to $G_4TSPB^-(toluene)_3(dioxane)$; (pink) $G_4TSPB^-(dioxane)_5$ single crystal after immersion for four hours in nitrobenzene, transforming to $G_4TSPB^-(nitrobenzene)_{1.5}$; (black at top) $G_4TSPB^-(dioxane)_5$ single crystal after immersion for four hours in aniline, transforming to $G_4TSPB^-(aniline)_5$. NMR solvent: dimethylsulfoxide.

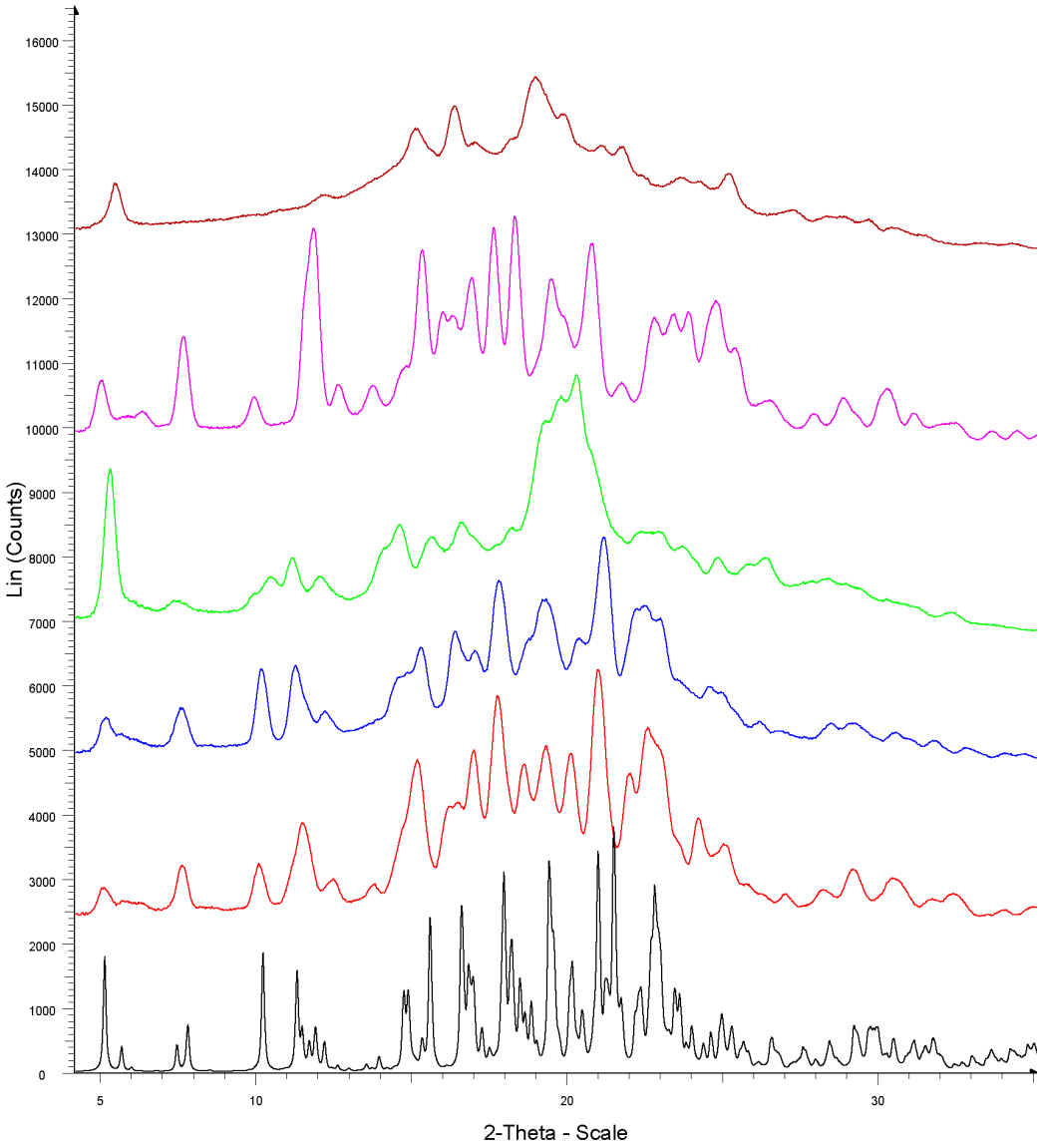

Figure S9. Powder X-ray diffraction of G_4TSPB samples after exchange with various guests. From bottom to top: (black) Powder diffraction pattern calculated from single crystal structure of $G_4TSPB\cdot(dioxane)_5$; (red) experimental powder diffraction pattern of $G_4TSPB\cdot(dioxane)_5$; (blue) after immersion in THF for four hours; (green) after immersion in aniline for four hours, (purple) after immersion in toluene for four hours; (brown) after immersion in nitrobenzene for four hours.

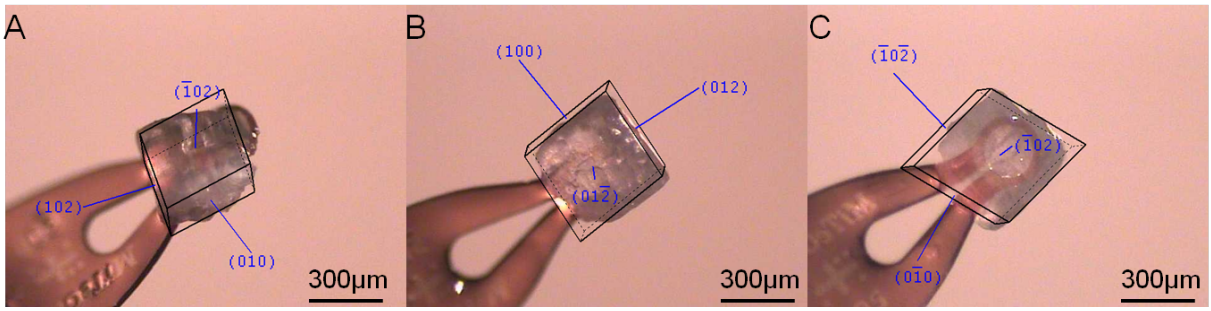

Figure S10. (A) Crystal of $G_4TSPB^-(dioxane)_5$ and indexed faces. (B) Crystal from A after immersion in THF for four hours, transforming to $G_4TSPB^-(THF)_5$. (C) Crystal from B after immersion in dioxane for four hours, reverting back to $G_4TSPB^-(dioxane)_5$.

Table S2. Crystallographic information for crystals A, B and C mentioned in Figure S10.

compound	$G_4TSPB^-(dioxane)_5$	$G_4TSPB^-(THF)_5$	$G_4TSPB^-(dioxane)_5$
crystal system	Triclinic	Triclinic	Triclinic
space group	*P*1	*P1*	*P*1
a (Å)	16.068(4)	12.043(5)	16.19
b (Å)	18.326(4)	15.891(6)	18.47
c (Å)	35.252(8)	34.087(13)	35.49
α (deg)	80.336(3)	84.671(5)	80.16
β (deg)	85.481(3)	87.393(5)	85.55
γ (deg)	77.775(3)	83.725(4)	77.67
V (Å^3)	9990.95	6452.18	10204
temp (K)	100(2)	100(2)	100(2)
Z	6	4	\
R_1 [$I > 2\sigma(I)$]	0.1302	0.1405	\

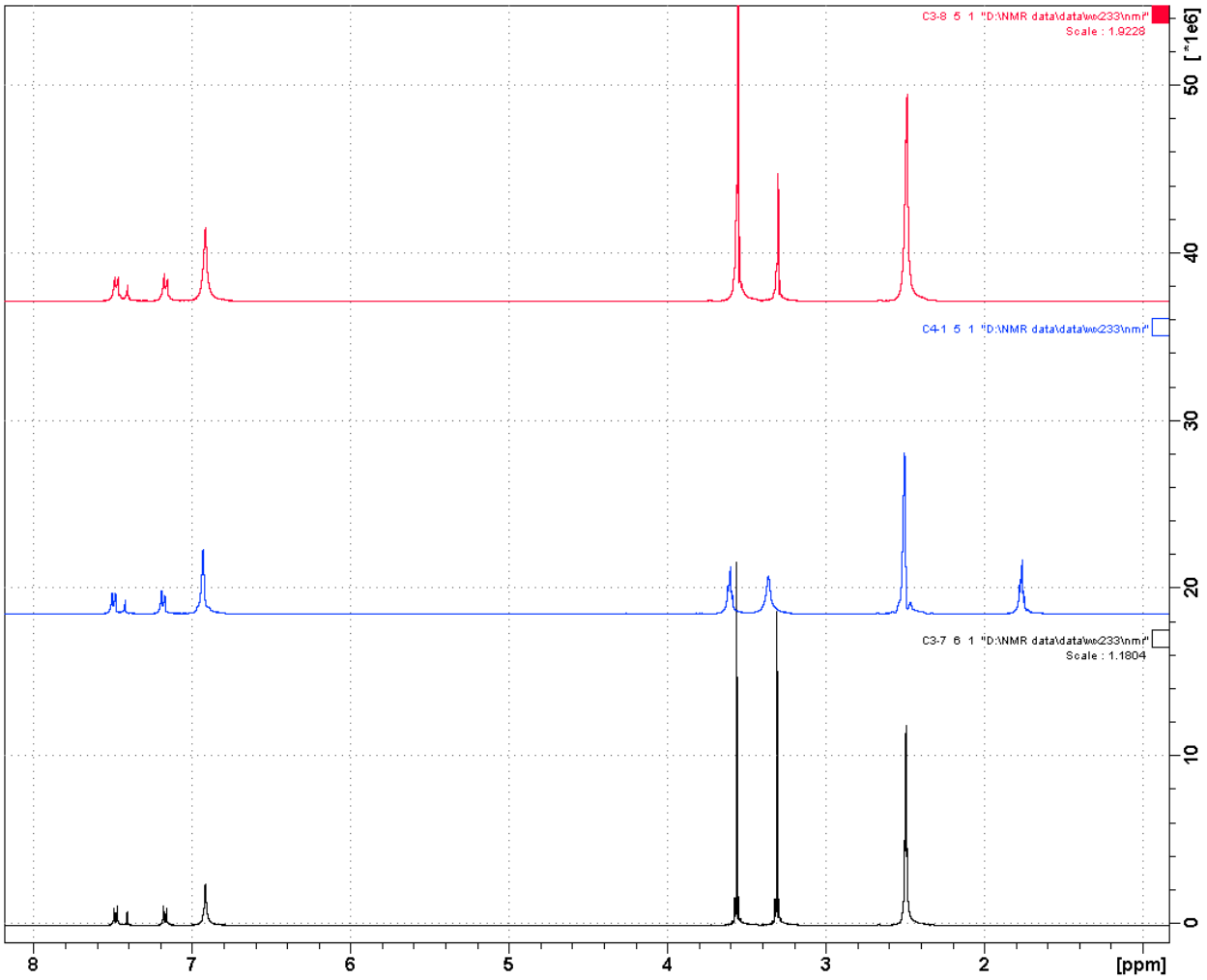

Figure S11. From bottom to top: (black) NMR spectrum of a $G_4TSPB^{\cdot}(dioxane)_5$ single crystal; (blue) $G_4TSPB^{\cdot}(dioxane)_5$ single crystal after immersion in THF for four hours, transforming to $G_4TSPB^{\cdot}(THF)_5$; (red) the $G_4TSPB^{\cdot}(THF)_5$ crystal after immersion in dioxane for four hours, reverting to $G_4TSPB^{\cdot}(dioxane)_5$. NMR solvent: dimethylsulfoxide.

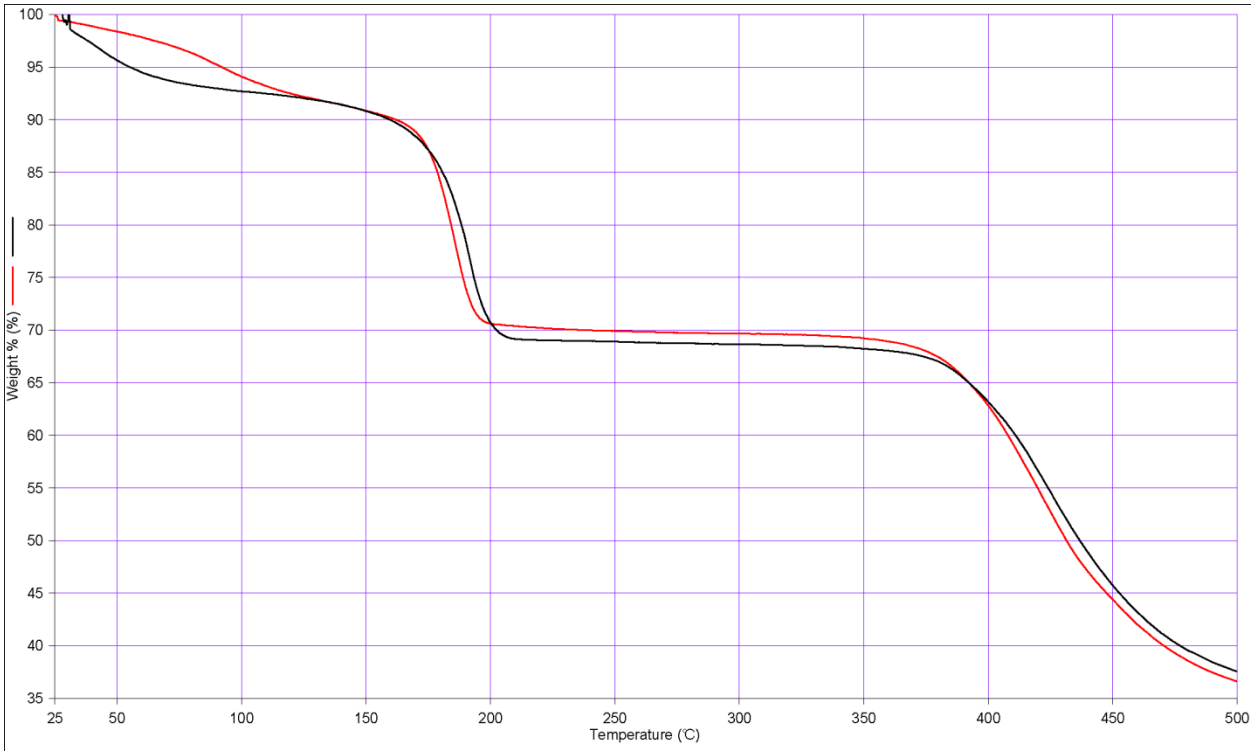

Figure S12. (black curve) TGA of $G_4TSPB^-(dioxane)_5$; (red curve) $G_4TSPB^-(THF)_5$. Heating rate = 10 ^oC/min.

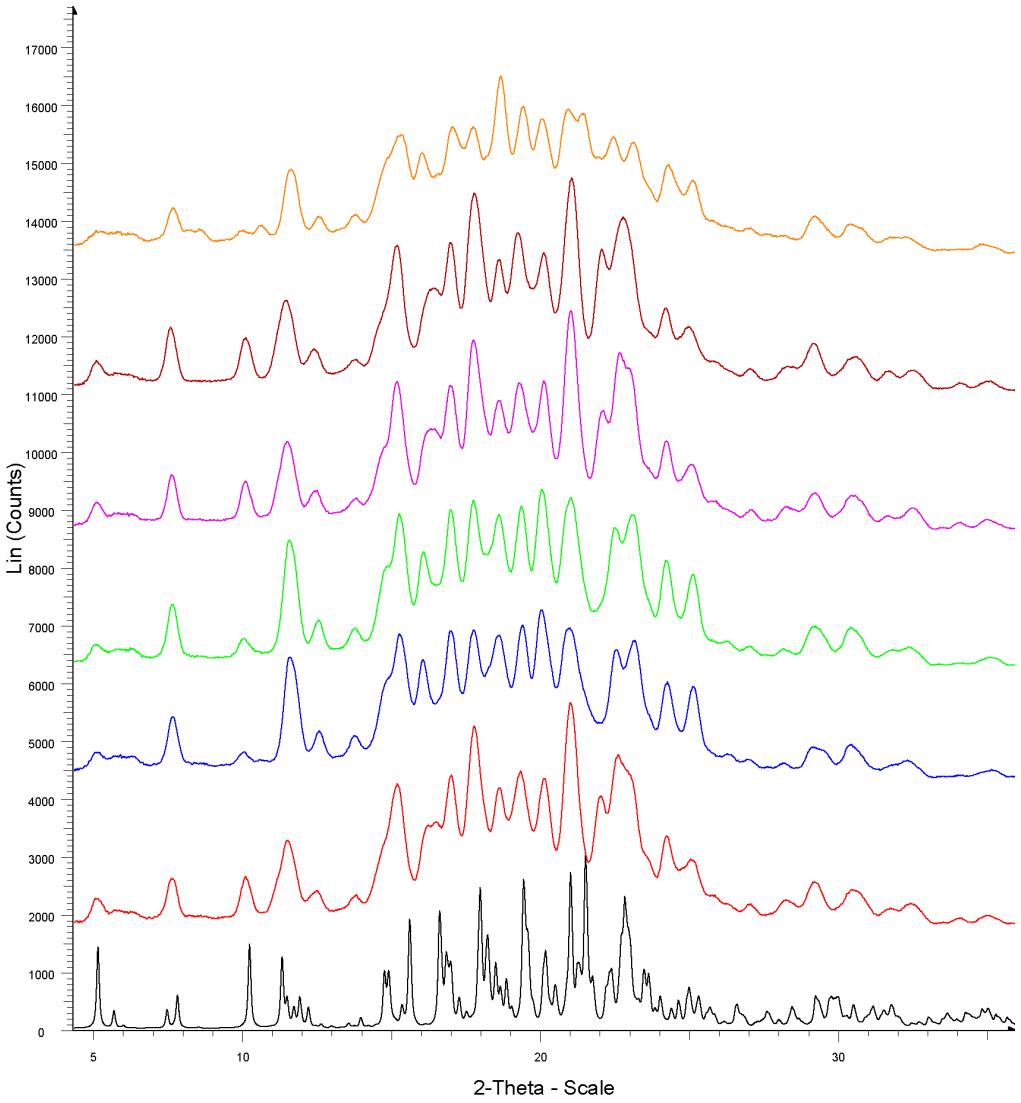

Figure S13. Powder X-ray diffraction illustrating the reversibility of transformation between $G_4TSPB^-(dioxane)_5$ and $G_4TSPB^-(THF)_5$. From bottom to top: (black) Powder pattern calculated from the single crystal structure of $G_4TSPB^-(dioxane)_5$; (red) $G_4TSPB^-(dioxane)_5$ after immersion in THF for four hours followed by immersion in dioxane for four hours; (blue) first repetition of the same cycle; (green) second repetition of the same cycle; (purple) third repetition of the same cycle; (brown) fourth repetition of the same cycle.

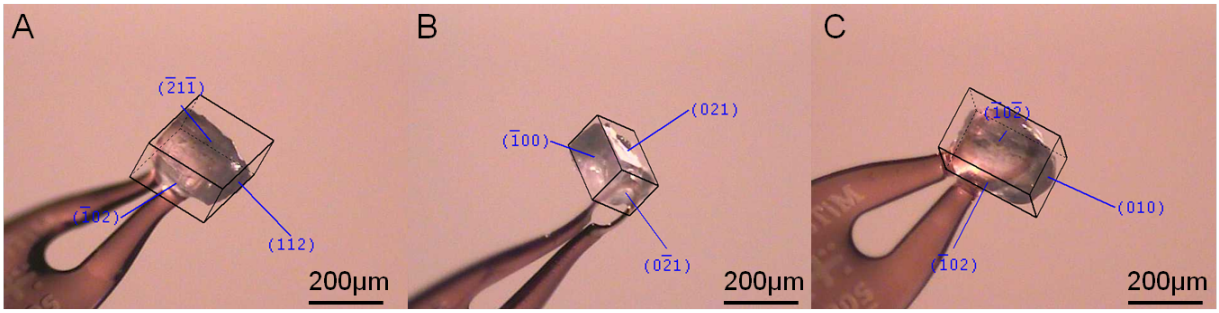

Figure S14. (A) Crystal of $G_4TSPB^-(dioxane)_5$ and indexed faces. (B) Crystal from A after immersion in toluene for four hours, transforming to $G_4TSPB^-(toluene)_3(dioxane)$. (C) Crystal from B after immersion in dioxane for four hours, reverting back to $G_4TSPB^-(dioxane)_5$.

Table S3. Crystallographic information for crystals A, B and C in Figure S14.

compound	$G_4TSPB^-(dioxane)_5$	$G_4TSPB^-(toluene)_3(dioxane)$	$G_4TSPB^-(dioxane)_5$
crystal system	Triclinic	Monoclinic	Triclinic
space group	*P*1	$P2_1$	*P*1
a (Å)	16.068(4)	6.1781(11)	16.21
b (Å)	18.326(4)	35.439(6)	18.47
c (Å)	35.252(8)	15.264(3)	35.63
α (deg)	80.336(3)	90	80.20
β (deg)	85.481(3)	100.518(3)	85.71
γ (deg)	77.775(3)	90	77.96
V (Å^3)	9990.95	3285.83	10269
temp (K)	100(2)	100(2)	100(2)
Z	6	2	\
R_1 [$I > 2\sigma(I)$]	0.1302	0.094	\

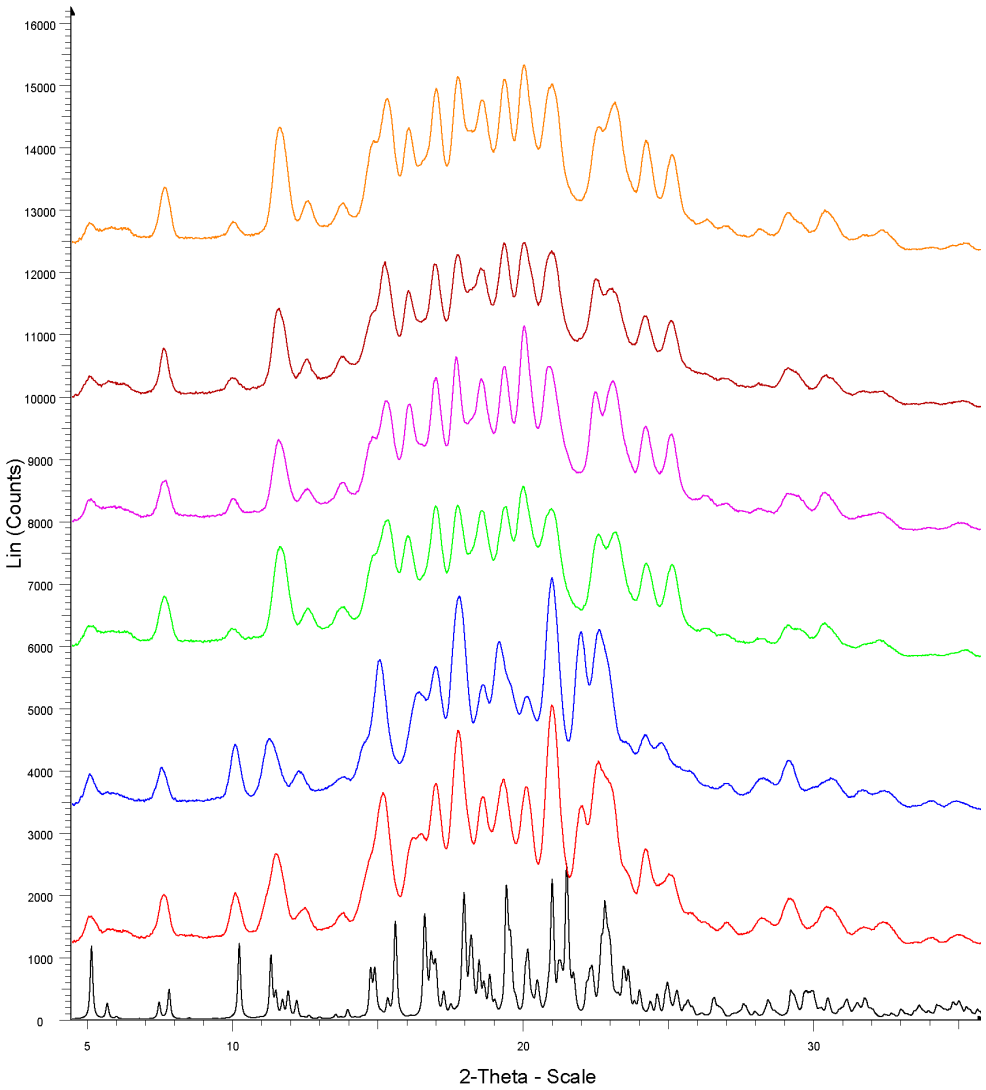

Figure S15. Powder X-ray diffraction illustrating the reversibility of transformation between $G_4TSPB^-(dioxane)_5$ and $G_4TSPB^-(toluene)_3(dioxane)$. From bottom to top: (black) Powder pattern calculated from the single crystal structure of $G_4TSPB^-(dioxane)_5$; (red) $G_4TSPB^-(dioxane)_5$ after immersion in toluene for four hours followed by immersion in dioxane for four hours; (blue) first repetition of the same cycle; (green) second repetition of the same cycle; (purple) third repetition of the same cycle; (brown) fourth repetition of the same cycle.

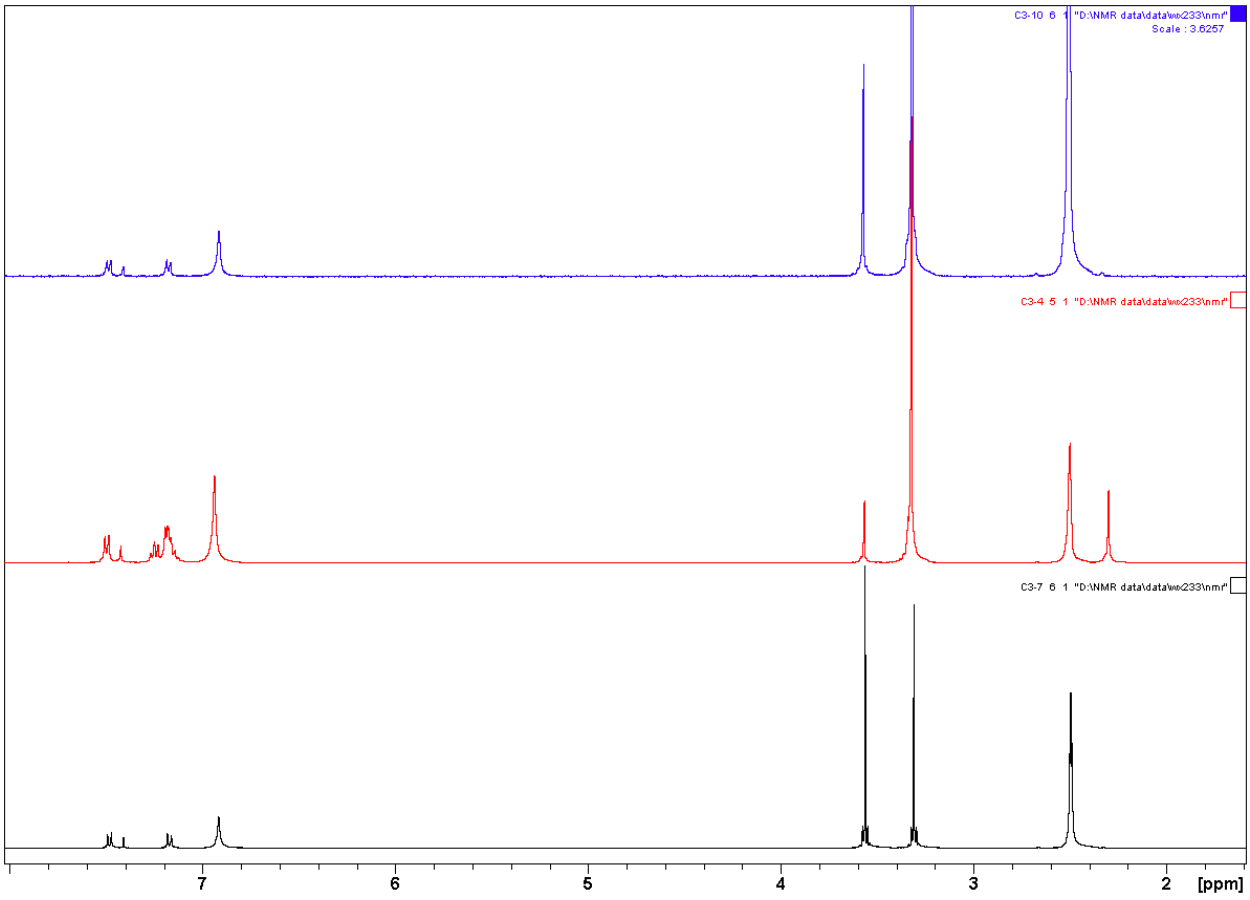

Figure S16. From bottom to top: (black) NMR spectrum of a $G_4TSPB^-(dioxane)_5$ single crystal; (red) $G_4TSPB^-(dioxane)_5$ single crystal after immersion in toluene for four hours, transforming to $G_4TSPB^-(toluene)_3(dioxane)$; (blue) $G_4TSPB^-(toluene)_3(dioxane)$ crystal after immersion in dioxane for four hours, reverting to $G_4TSPB^-(dioxane)_5$. NMR solvent: dimethylsulfoxide.

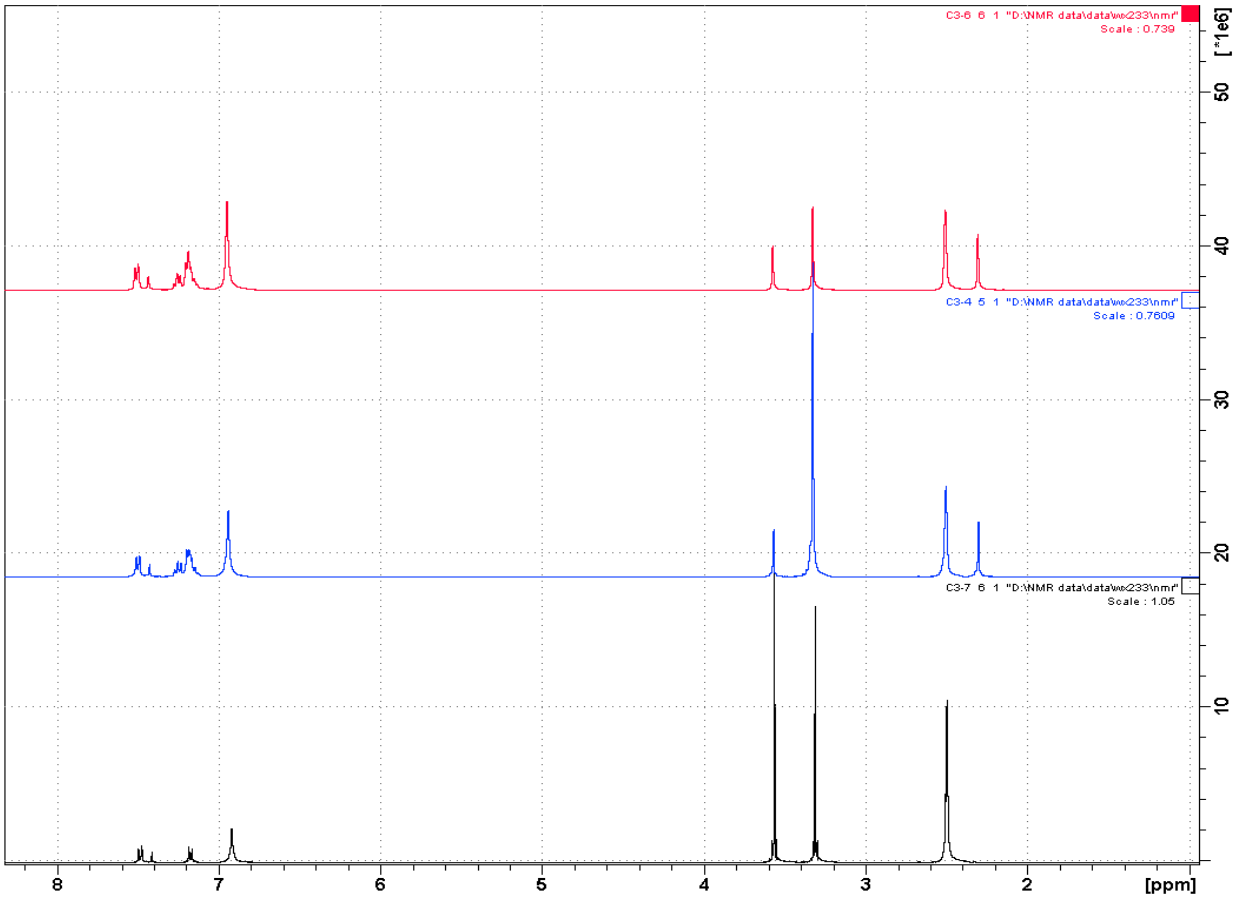

Figure S17. From bottom to top: (black) NMR spectrum of a $G_4TSPB^-(dioxane)_5$ single crystal; (blue) $G_4TSPB^-(dioxane)_5$ single crystal after immersion in toluene for one day, transforming to $G_4TSPB^-(toluene)_3(dioxane)$; (red) $G_4TSPB^-(dioxane)_5$ single crystal after immersion in toluene for nine days, transforming to $G_4TSPB^-(toluene)_3(dioxane)$ but with no further exchange with toluene. NMR solvent: dimethylsulfoxide.

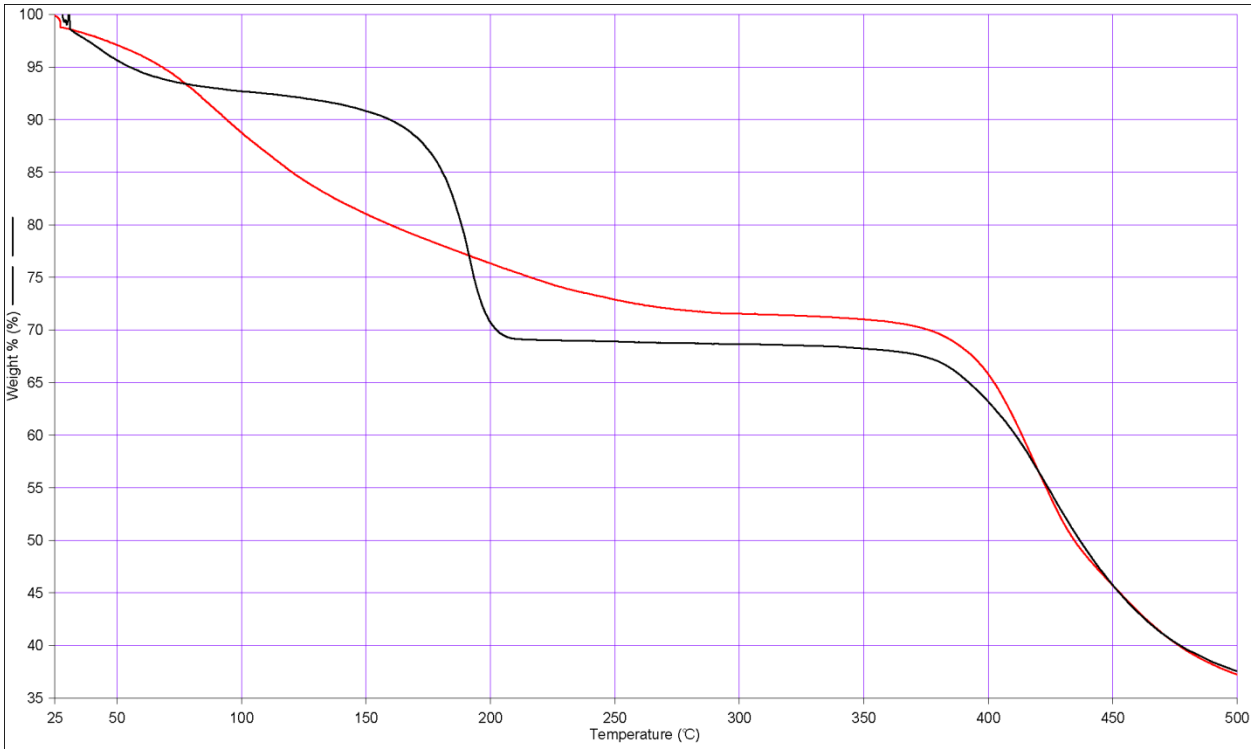

Figure S18. (black curve) TGA of $G_4TSPB^-(dioxane)_5$; (red curve) $G_4TSPB^-(toluene)_3(dioxane)$. Heating rate = 10 ^oC/min.

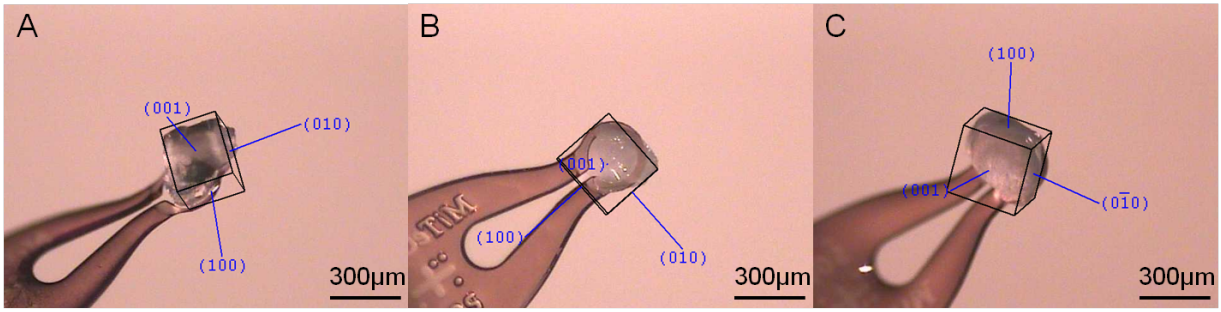

Figure S19. (A) Crystal of $G_4TSPB^-(THF)_5$ and indexed faces. (B) Crystal from A after immersion in toluene for four hours, transforming to $G_4TSPB^-(toluene)_3(THF)_{0.5}$. (C) Crystal from B after immersion in dioxane for four hours, reverting to $G_4TSPB^-(THF)_5$.

Table S4. Crystallographic information for crystals A, B and C in Figure S19.

compound	$G_4TSPB^-(THF)_5$	$G_4TSPB^-(toluene)_3(THF)_{0.5}$	$G_4TSPB^-(THF)_5$
crystal system	Triclinic	Monoclinic	Triclinic
space group	*P*1	\	*P*1
a (Å)	12.043(5)	30.01	12.18
b (Å)	15.891(6)	6.29	16.03
c (Å)	34.087(13)	35.74	34.42
α (deg)	84.671(5)	90	85.02
β (deg)	87.393(5)	94.69	88.51
γ (deg)	83.725(4)	90	83.48
V (Å^3)	6452.18	6720	6627
temp (K)	100(2)	100(2)	100(2)
Z	4	4	4
R_1 [$I > 2\sigma(I)$]	0.1405	\	\

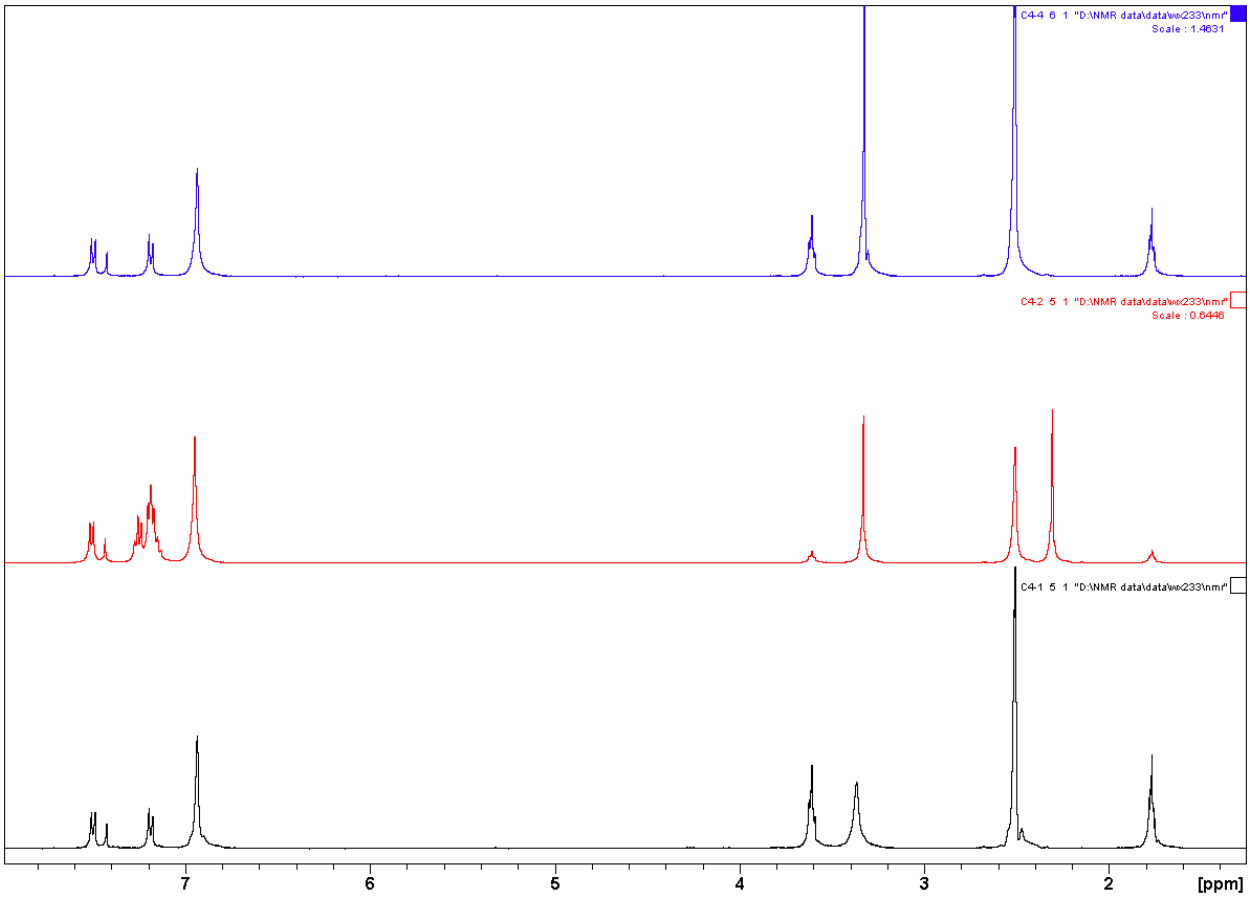

Figure S20. From bottom to top: (black) NMR spectrum of a $G_4TSPB^-(THF)_5$ single crystal; (red) $G_4TSPB^-(THF)_5$ single crystal after immersion in toluene for four hours, transforming to $G_4TSPB^-(toluene)_3(THF)_{0.5}$; (blue) $G_4TSPB^-(toluene)_3(THF)_{0.5}$ single crystal after immersion in THF for four hours, reverting to $G_4TSPB^-(THF)_5$. NMR solvent: dimethylsulfoxide.

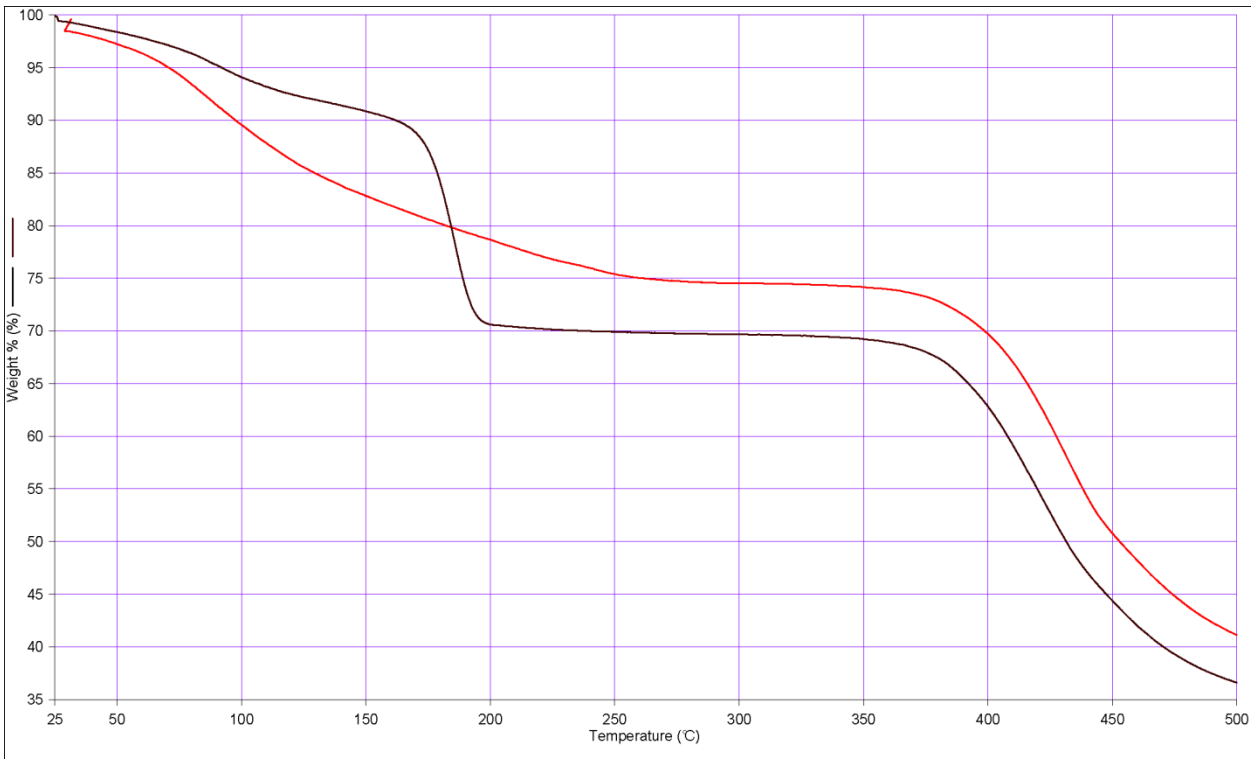

Figure S21. (black curve) TGA of $G_4TSPB^{-}(THF)_5$; (red curve) $G_4TSPB^{-}(toluene)_3(THF)_{0.5}$. Heating rate = 10 ^{o}C/min.

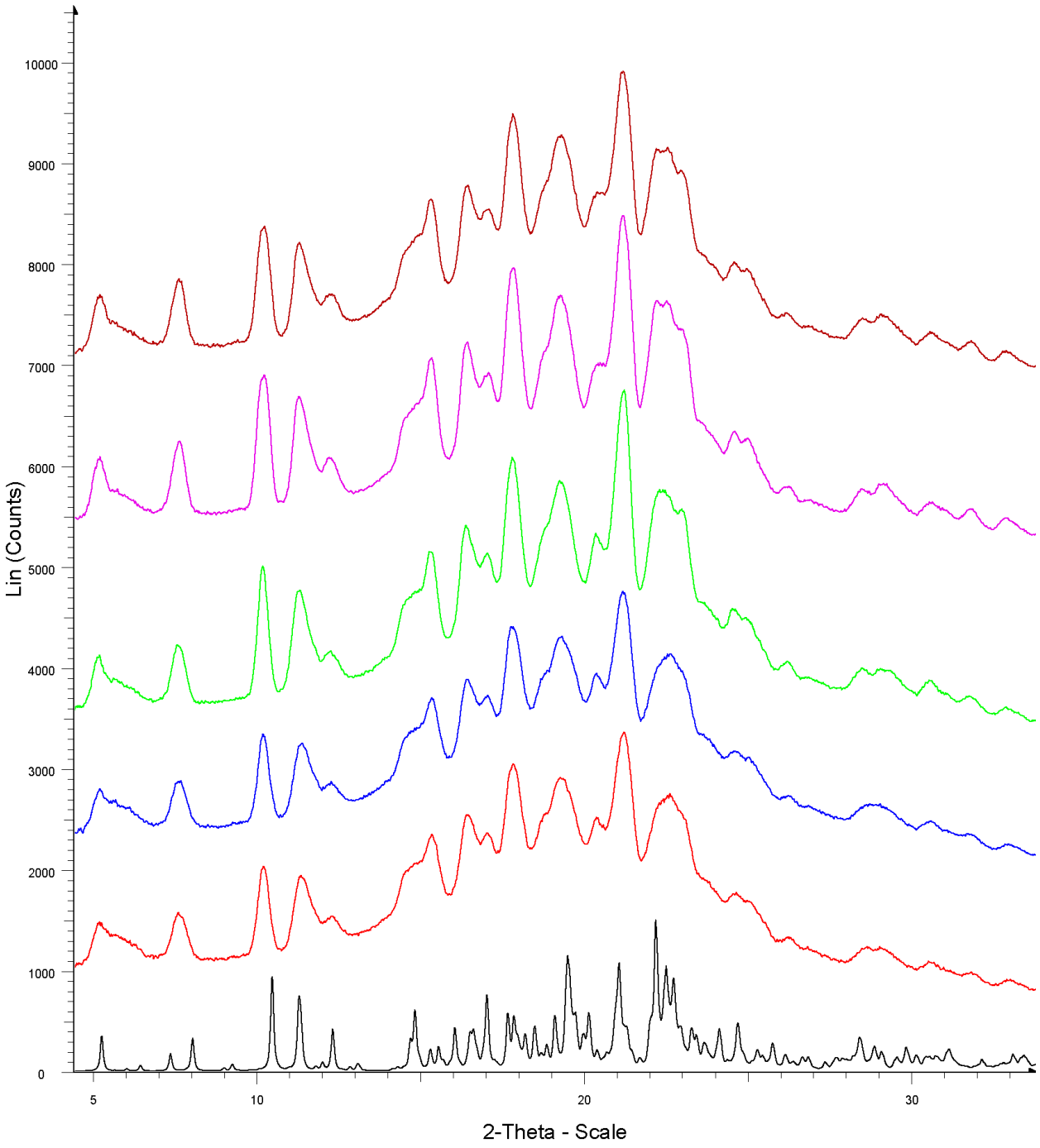

Figure S22. Powder X-ray diffraction illustrating the reversibility of transformation between $G_4TSPB^{\cdot}(THF)_5$ and $G_4TSPB^{\cdot}(toluene)_3(THF)_{0.5}$. From bottom to top: (black) Powder pattern calculated from the single crystal structure of $G_4TSPB^{\cdot}(THF)_5$; (red) $G_4TSPB^{\cdot}(THF)_5$ after immersion in toluene for four hours followed by immersion in THF for four hours; (blue) first repetition of the same cycle; (green) second repetition of the same cycle; (purple) third repetition of the same cycle; (brown) fourth repetition of the same cycle.

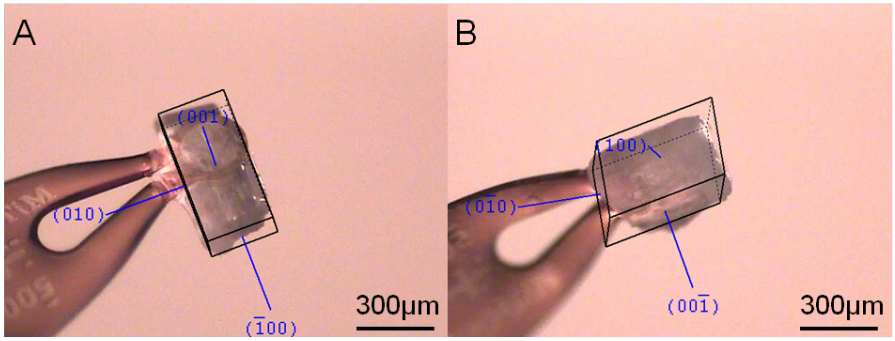

Figure S23. (A) Crystal of $G_4TSPB^-(toluene)_3(dioxane)$ and indexed faces. (B) Crystal from A after immersion in THF for four hours, transforming to $G_4TSPB^-(THF)_5$.

Table S5. Crystallographic information for crystals A and B in Figure S23.

compound	$G_4TSPB^-(toluene)_3(dioxane)$	$G_4TSPB^-(THF)_5$
crystal system	Monoclinic	Triclinic
space group	$P2_1$	*P1*
a (Å)	6.25	12.12
b (Å)	35.74	16.09
c (Å)	15.38	34.40
α (deg)	90	84.85
β (deg)	100.65	87.19
γ (deg)	90	83.63
V (Å^3)	3375	6634
temp (K)	100(2)	100(2)

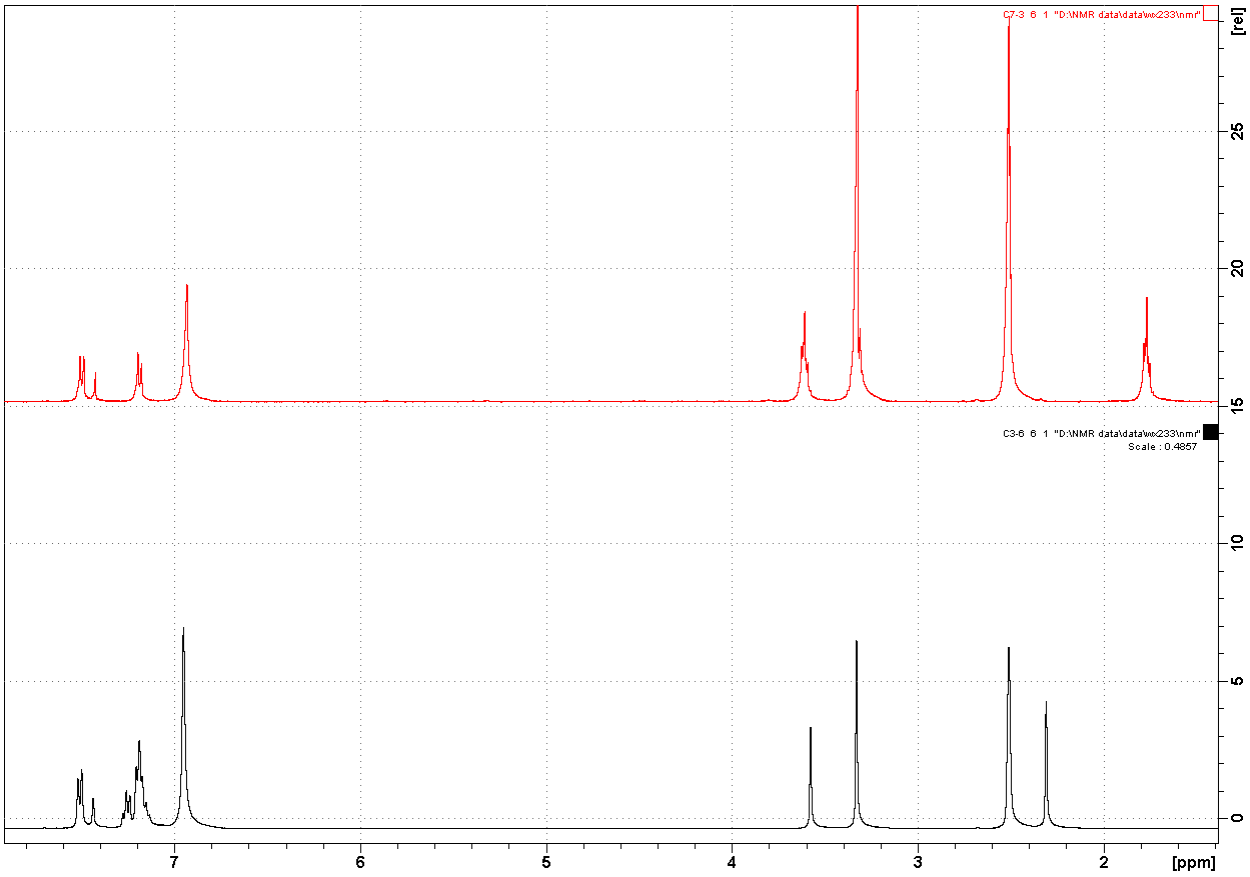

Figure S24. From bottom to top: (black) NMR spectrum of a $G_4TSPB^-(toluene)_3(dioxane)$ single crystal; (red) $G_4TSPB^-(toluene)_3(dioxane)$ single crystal after immersion in THF for four hours, transforming to $G_4TSPB^-(THF)_5$. NMR solvent: dimethylsulfoxide.

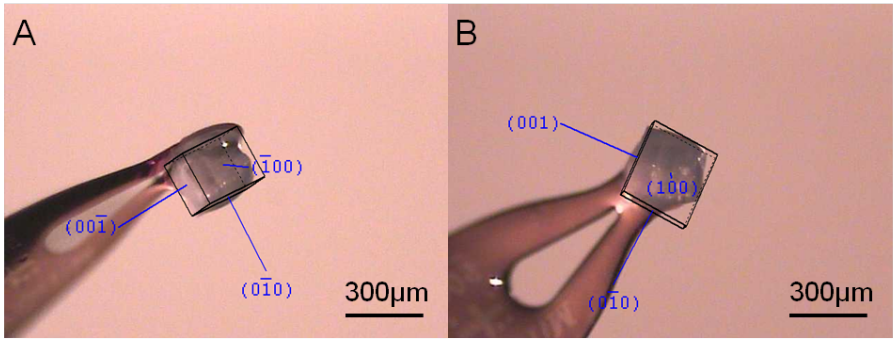

Figure S25. (A) Crystal of $G_4TSPB^-(toluene)_3(THF)_{0.5}$ and indexed faces. (B) Crystal from A after immersion in dioxane for four hours, transforming to $G_4TSPB^-(dioxane)_5$.

Table S6. Crystallographic information for crystals A and B in Figure S25.

compound	$G_4TSPB^-(toluene)_3(THF)_{0.5}$	$G_4TSPB^-(dioxane)_5$
crystal system	Monoclinic	Triclinic
space group	/	*P1*
a (Å)	30.18	16.20
b (Å)	6.29	18.48
c (Å)	35.68	35.70
α (deg)	90	86.26
β (deg)	94.41	89.32
γ (deg)	90	77.97
V (Å^3)	6758	10435
temp (K)	100(2)	100(2)

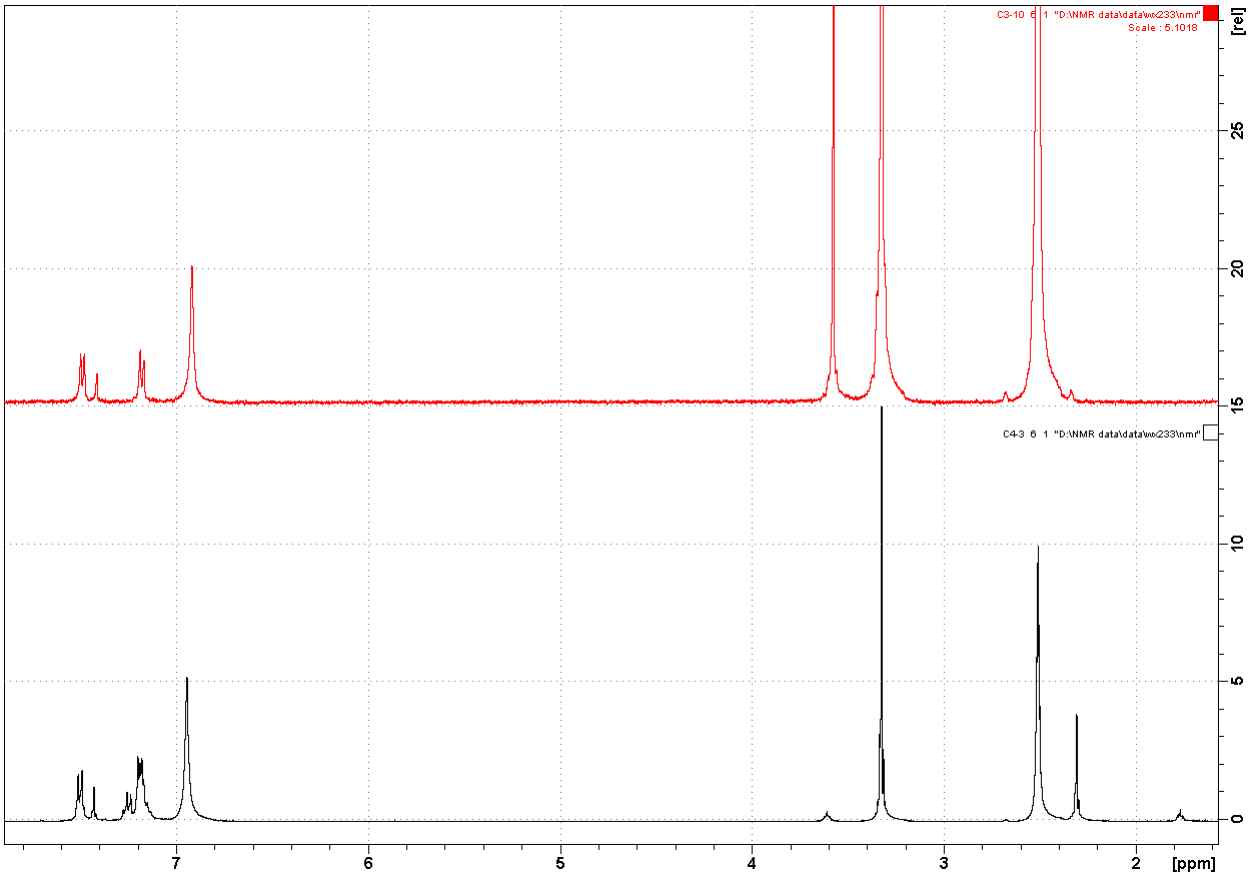

Figure S26. From bottom to top: (black) NMR spectrum of a $G_4TSPB^-(toluene)_3(THF)_{0.5}$ single crystal; (red) $G_4TSPB^-(toluene)_3(THF)_{0.5}$ single crystal after immersion in dioxane for four hours, transforming to $G_4TSPB^-(dioxane)_5$. NMR solvent: dimethylsulfoxide.

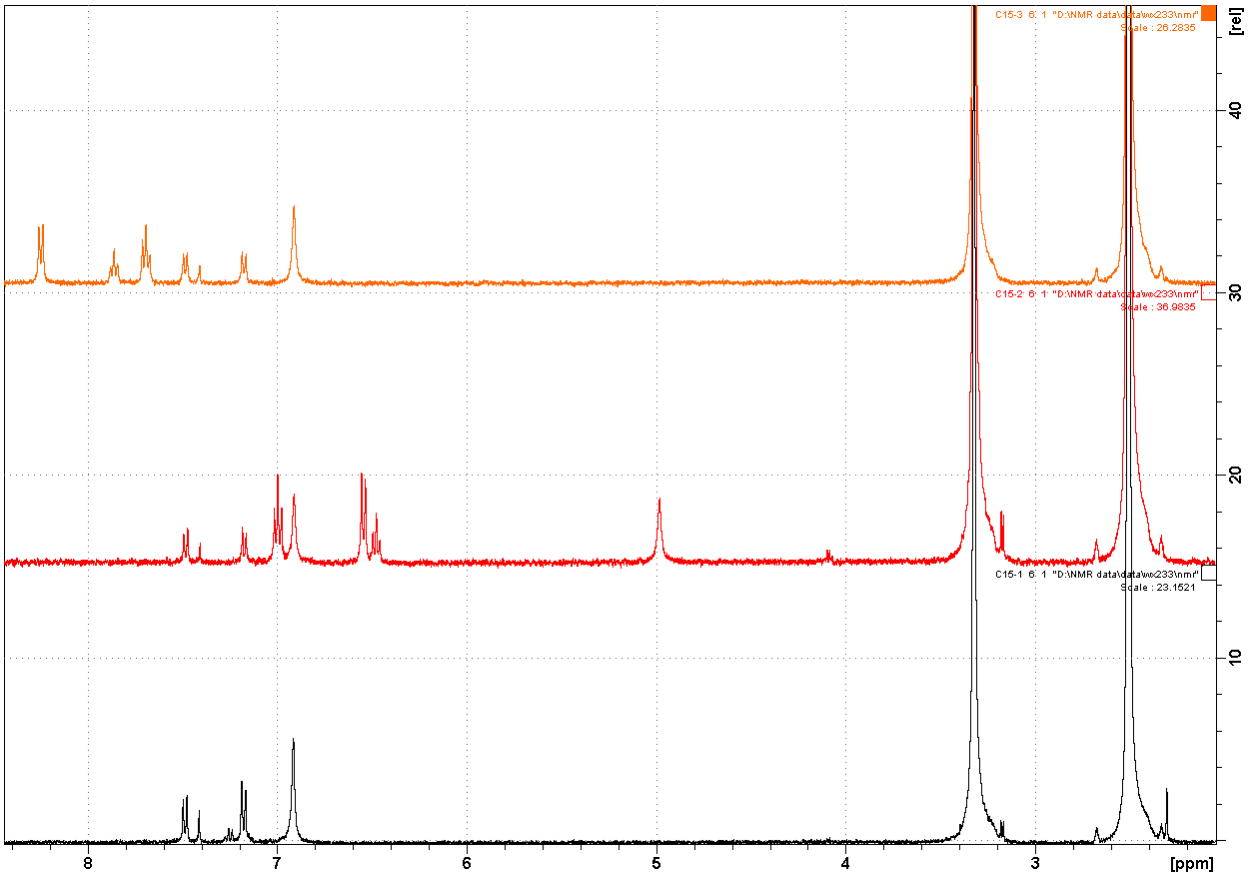

Figure S27. From bottom to top: (black) NMR spectrum of G_4TSPB precipitate formed by layering toluene on a methanol solution of G_4TSPB; (red) G_4TSPB precipitate formed by layering a methanol solution of G_4TSPB on aniline; (orange) G_4TSPB precipitate formed by layering a methanol solution of G_4TSPB on nitrobenzene. NMR solvent: dimethylsulfoxide.Attempts to grow single crystals of toluene, aniline and nitrobenzene inclusion compounds were not successful.

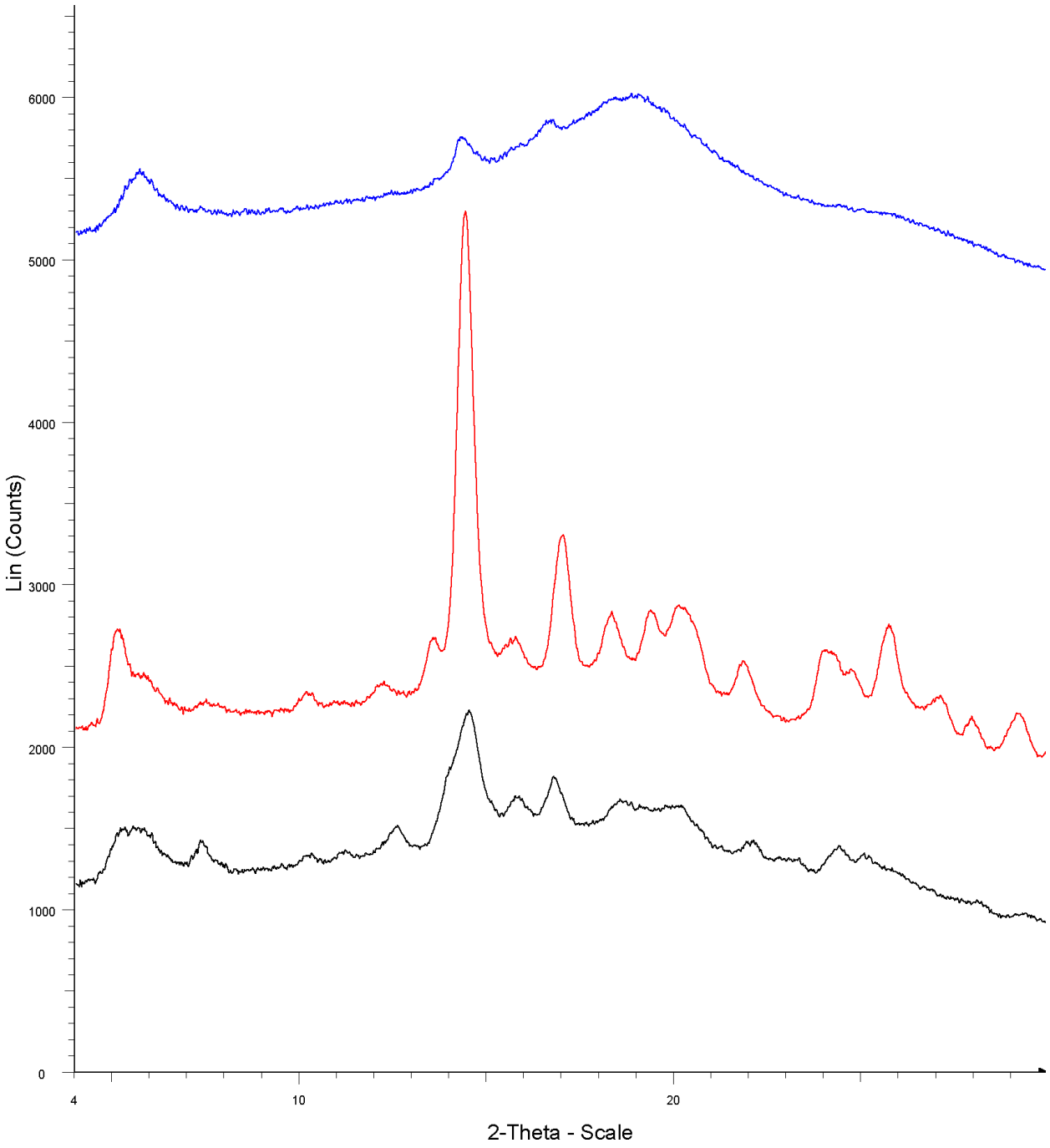

Figure S28. (black) Powder X-ray diffraction characterization of G_4TSPB precipitate formed by layering toluene on a methanol solution of G_4TSPB; (red) G_4TSPB precipitate formed by layering a methanol solution of G_4TSPB on aniline; (blue) G_4TSPB precipitate formed by layering a methanol solution of G_4TSPB on nitrobenzene.

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