Lithium achieves sequence selective ring-opening terpolymerisation (ROTERP) of ternary monomer mixtures

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Section S1: Methods

Solvents and reagents were obtained from commercial sources and used as received unless stated otherwise. If “dried solvents” were used these were obtained by different procedures. Toluene, EtOH, n-hexane, n-pentane and CH2Cl2 were prepared by using an MBraun Solvent Purification System MB-SPS 800 filled with Al2O3. Et2O was dried over Na/benzophenone and THF was dried over K/benzophenone under argon. The CDCl3 was dried over CaH2 and d8-THF over sodium prior to vacuum transfer onto 4 Å sieves followed by three freeze pump thaw degassing cycles. 1H, 13C{1H}, and 7Li NMR spectra were recorded by using a Jeol JNM-ECA 400II, Bruker Advance 600 and 700 MHz spectrometer. 1H and 13C{1H} chemical shifts are referenced to the residual proton resonance of the deuterated solvents and 7Li{1H} chemical shifts are referenced to an internal reference capillary containing LiO3SCF3 in d6-acetone (alongside a PPh3 31P reference and PhF 19F reference).

Epoxides, CS2 and ε-DL were dried over calcium hydride at room temperature for 3 days, vacuum transferred (for CHO and ε-DL fractionally distilled under static vacuum) followed by three freeze pump thaw degassing cycles and stored inside an argon filled glovebox prior to use. Phtalic thioanhydride was synthesized according to the literature procedure and (for runs Table 1 #5 and #6) this was then purified by recrystallisation from tBuOMe followed by recrystallisation from CHCl3 and two sublimation under dynamic vacuum at 90°C and was stored inside a argon filled glovebox prior to use.[1]

UV-visible spectra were collected on a Varian Cary 50 UV spectrometer.

Infrared spectra were measured using a Thermo-Nicolet Nexus 670 FTIR spectrometer with DuraSamp IR accessory in total reflection at room temperature.

The molecular mass and polydispersity of the polymers were determined by a Waters 1515 size exclusion chromatography (SEC) instrument equipped with two linear PLgel columns (Mixed-C) following a guard column and a differential refractive index detector using tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min at 30 °C and a series of narrow polystyrene standards for the calibration of the columns. Each polymer sample was dissolved in HPLC-grade THF (6 mg/mL) and filtered through a 0.20 μm porous frit prior to analysis.

Polymer films for refractive index determination were spun from a Vacuum Spin Coater (SCE 150). 100 μL of terpolymers in CH2Cl2 (20 mg/mL) was dropped onto a silicon slice and the speed of the spin coater was then raised to 3000 r/min lasting for 1 min, affording a film of approximately 100 – 200 nm. Spectroscopic ellipsometry (SE) was performed on a SENpro ellipsometer (wavelength 350 – 1050 nm) and evaluated with SpectraRay 3 (Version 5.3.2.1853) software from SENTECH instruments GmbH (Berlin, Germany).

High-resolution ESI mass spectra were obtained using a Waters UPLC-Synapt G2-S HDMS.
Section S2: ROTERP procedure and details

Terpolymerization protocol: In an argon-filled glovebox, LiHMDS (an optionally BnOH) was dissolved in butylene oxide and the mixture was transferred to a flame dried vial equipped with a flame dried stirrer bar and sealed with a melamine cap containing a Teflon inlay. CS$_2$ and PTA were then added and the vial was brought outside the glovebox and placed in a pre-heated oil bath at 80°C for the specified time. In cases where the reaction progress was monitored, the vial was rapidly cooled to room temperature with a dry ice cooling bath and brought inside an argon-filled glovebox before the aliquot was remove. At the specified end point of the reaction, the polymer was isolated by adding the polymerisation mixture to 200 mL of acidified MeOH (20 µL concentrated HCl per 200 mL MeOH) resulting in the precipitation of the yellow product. After two further precipitations from DCM/MeOH, the polymer was isolated by filtration and dried in a vacuum oven set to 60 °C.
Section S3: Polymer characterisation data

Figure S1: $^{13}$C{$^{1}$H} NMR spectrum (126 MHz, CDCl$_3$, 25°C) of terpolymer corresponding to table 1, run #3.

Figure S2: Zoom into carbonyl region of the $^{13}$C{$^{1}$H} NMR spectrum (126 MHz, CDCl$_3$, 25°C) of terpolymer corresponding to table 1, run #3.
Figure S 3: $^1$H – $^{13}$C HMBC NMR spectrum (CDCl$_3$, 25°C) of terpolymer corresponding to table 1, run #3.

Figure S 4: DSC heating curve of terpolymer corresponding to table 1, run #4.
Figure S 5: FT ATRIR Spectrum of PTA/BO/CS$_2$ terpolymer corresponding to table 1, run #4.

Figure S 6a: Zoom into the UVVIS spectrum (DCM, 25°C) of terpolymer corresponding to table 1, run #4.
Figure S 6b: Zoom into the end-group resonances of (left) a ROTERP reaction initiated from LiOBn and (right) initiated from LiHMDS.

Figure S 6c: DOSY NMR spectrum (126 MHz, CDCl₃, 25°C) of terpolymer corresponding to table 1, run #3
Figure S 7: TGA of terpolymer corresponding to table 1, run #4.

Figure S 8: $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25°C) of terpolymer corresponding to table 1, run #9.
Figure S 9: $^{13}$C($^1$H) NMR spectrum (126 MHz, CDCl$_3$, 25°C) of terpolymer corresponding to table 1, run #9.

Figure S 10: Zoom into carbonyl region of the $^{13}$C($^1$H) NMR spectrum (126 MHz, CDCl$_3$, 25°C) of terpolymer corresponding to table 1, run #9.
Figure S 11: $^1$H – $^1$H COSY NMR spectrum (CDCl$_3$, 25°C) of terpolymer corresponding to table 1, run #9.

Figure S 12: $^1$H – $^{13}$C HMBC NMR spectrum (CDCl$_3$, 25°C) of terpolymer corresponding to table 1, run #9.
**Figure S 13:** DSC heating curve of terpolymer corresponding to table 1, run #9.

**Figure S 14:** Comparison of the aromatic region of the $^1$H NMR spectra (400 MHz, CDCl$_3$, 25°C) of terpolymers corresponding to table 1, run #7 to #10.
Figure S15: Comparison of the aromatic region of the $^1\text{H}$ NMR spectra (400 MHz, CDCl$_3$, 25°C) of crude terpolymers obtained at different reaction temperatures (loading as per Table 1 run #9).

Figure S16: $^1\text{H}$ NMR spectra (400 MHz, CDCl$_3$, 25°C) of terpolymers corresponding to Table 1 run #12.
Figure S 17: $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25°C) of copolymer corresponding to table 1, run #15.

Figure S 18: $^{13}$C($^1$H) NMR spectrum (126 MHz, CDCl$_3$, 25°C) of copolymer corresponding to table 1, run #15. Due to significant transesterification and O/S
exchange process as well as the presence of ether linkages unambiguous assignment was not possible.

**Figure S 19:** $^1$H - $^{13}$C HMBC NMR spectrum (CDCl$_3$, 25°C) of copolymer corresponding to table 1, run #15.

**Figure S 20:** Zoom into the $^1$H - $^{13}$C HMBC NMR spectrum (CDCl$_3$, 25°C) of copolymer corresponding to table 1, run #15.
Figure S 21: FT ATR-IR spectrum of copolymer corresponding to table 1, run #9.

Figure S 22: $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25°C) of reaction mixture produced according to Table 1, #14.
Figure S 23: $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25°C) of aliquots removed at different stages of ROTERP corresponding to table 1, run #9.

Figure S 24: TGA of CS$_2$/PO copolymer reported in this study obtained from the reaction of 1 LiHMDS: 500 PO : 1000 CS$_2$ at 25°C for 16h.
Section S4: SEC traces

Figure S 25: SEC traces of polymers reported in this study.
Figure S 26: SEC traces of polymers reported in this study.
Figure S 27: Development of molecular masses and polydispersity of terpolymer corresponding to table 1, run #9.
Section S5: Synthesis, characterisation and reactivity of model MTC

![Chemical structure of MTC][1]

**Synthesis of MTC**: Inside an Argon filled glovebox, phthalic thioanhydride (164.2 mg, 1.00 mmol) and LiO'Bu (80.0 mg, 1.00 mmol) were loaded into an oven dried Schlenk fask, brought outside the glovebox and connected to an Schlenkline. Dry THF (25mL) was added and the mixture was stirred overnight giving an orange solution. All volatiles were removed in vacuum yielding MTC·THF as a yellow solid (300.0 mg, 0.95 mmol, 95%). XRD quality crystals were grown by layering a saturated THF solution with Pentane.

**¹H NMR (400 MHz, d₈-THF, 25°C)**; δ(ppm): 7.77 (dd, J = 7.5, 1.1 Hz, 1H, H₄), 7.35 (dd, J = 7.5, 1.1 Hz, 1H, H₁), 7.25 (td, J = 7.5, 1.4 Hz, 1H, H₂), 7.16 (td, J = 7.5, 1.3 Hz, 1H, H₃), 3.65 – 3.53 (m, 4H, THF), 1.86 – 1.71 (m, 4H, THF), 1.52 (s, 6H, tBu).

**¹³C{¹H} NMR (101 MHz, d₈-THF, 25°C)**; δ(ppm): 218.63 (C₈), 169.33 (C₁), 149.04 (C₇), 131.31 (C₂), 129.61 (C₃), 129.47 (C₅), 128.06 (C₄), 127.24 (C₆), 80.81 (C₁₁), 68.02 (C₉), 28.08 (C₁₂), 26.13 (C₁₀).

**⁷Li NMR (156 MHz, d₈-THF, 25°C)**; δ(ppm): 0.63.

**FTIR [cm⁻¹]**: 1685.1 (Ester C=O), 1450.8 (Thiocarboxylate C=O)

**HRESI-MS (negative mode)**: m/z = calculated [M - Li]⁻ 237.0585. Found 237.0650
Figure S 28: $^1$H NMR spectrum (400 MHz, d$_8$-THF, 25°C) of MTC·THF.

Figure S 29: $^{13}$C($^1$H) NMR spectrum (101 MHz, d$_8$-THF, 25°C) of MTC.
**Figure S 30:** $^7$Li NMR spectrum (194 MHz, d$_8$-THF, 25°C) of MTC. Signal at 2.25 ppm corresponds to internal LiSO$_3$CF$_3$ standard.

**Figure S 31:** Solid state FT-ATIR spectrum of MTC.
In an oven dried J. Youngs NMR Tube MTC-THF (50.0 mg, 0.16 mmol, 1 eq.) dissolved in d$_8$-THF (0.6 mL) and BO (7.0 µL, 0.08 mmol, 0.5 equiv.) was let react for 10 min and analysed by NMR. The mixture was then let react for another 2h and analysed by NMR. Longer reaction times or more equivalents BO result in the appearance of broad signal under disappearance of the thiiran signals presumably due to competitive formation of polythioether.

**Figure S 32:** Overlaid $^1$H NMR (400 MHz, d$_8$-THF, 25°C) spectra of BO addition to MTC (top) 10 min after addition and (middle) 2h after addition and (bottom) carboxylate derivative of MTC prepared from 1 eq. LiO'Bu with phtalic anhydride.

**BO insertion from MTC:** Excess butylene oxide (1mL) was added to solid MTC-THF (50mg). The resulting mixture was stirred for 30 min at room temperature before all volatiles were removed in vacuum prior to spectroscopic analysis.
**Figure S 33:** $^1$H NMR spectrum (400 MHz, d$_8$-THF, 25°C) of BO insertion products of MTC.

**Figure S 34:** Zoom into the carbonyl region of the $^1$H-$^{13}$C HMBC NMR spectrum (d$_8$-THF, 25°C) of BO insertion of MTC.
Figure S 35: Solid state FTIR spectrum of BO insertion of MTC.

Figure S 36: Positive Mode HR-ESI MS of BO insertion products of MTC.
Figure S 37: UVVIS spectra before and after BO insertion of MTC in THF.

Reaction between MTC and BO in presence of CS$_2$: In an oven dried J. Youngs NMR Tube MTC·THF (50.0 mg, 0.16 mmol, 1 eq.) dissolved in d$_8$-THF (0.4 mL) and CS$_2$ (0.4 mL, 6.6 mmol, 42 equiv.) and BO (7.0 µL, 0.08 mmol, 0.5 equiv.) was added. The mixture was let react for 5 min and analysed by NMR.

Figure S 38: $^1$H NMR spectrum (400 MHz, d$_8$-THF, 25°C) of product mixture produced from the reaction of MTC with 1 eq. BO in presence of excess CS$_2$. 
Figure S 39: $^1$H-$^{13}$C HMBC NMR spectrum (d$_8$-THF, 25°C) of product mixture produced from the reaction of MTC with 1 eq. BO in presence of excess CS$_2$.

Synthesis of MTC$_{Na-0.75}$THF: Inside an Argon filled glovebox, phtalic thioanhydride (164.2 mg, 1.00 mmol) and NaO$i$Bu (96.0 mg, 1.00 mmol) were loaded into an oven-dried Schlenk flask, brought outside the glovebox and connected to an Schlenkline. Dry THF (25mL) was added, and the mixture was stirred overnight giving an orange suspension. All volatiles were removed in vacuum yielding MTC$_{Na}$ as a orange solid (298.3 mg, 0.95 mmol, 95%). XRD quality crystals were grown by layering the crude reaction mixture with pentane.

$^1$H NMR (400 MHz, d$_8$-THF, 25°C): $\delta$(ppm): 7.83 (d, $J = 7.5$ Hz, 1H, H-1), 7.35 – 7.14 (m, 4H, H-2/H-3/H-4), 3.82 – 3.37 (m, THF), 2.01 – 1.61 (m, THF), 1.48 (s, 9H, $^1$Bu).

Due to the insolubility of MTC$_{Na}$, $^{13}$C data was obtained via $^1$H-$^{13}$C HMBC NMR spectroscopy.
$^{13}$C($^1$H) NMR (101 MHz, $d_8$-THF, 25°C); δ(ppm): 209.92 (C1), 169.52 (C8), 148.29 (C2), 131.29 (C7), 129.45 (C6), 129.00 (C4), 127.41 (C5), 127.00 (C2), 80.28 (C9), 28.34 (C10)

FTIR [cm$^{-1}$]: 1684.0 (Ester C=O), 1451.6 (Thiocarboxylate C=O)

HRESI-MS (negative mode): m/z = calculated [M - Na]$^-$ 237.0585. Found 237.0545

Figure S 40: $^1$H NMR spectrum (400 MHz, $d_6$-DMSO, 25°C) of MTC$^{\text{Na}}·0.75$THF.

Figure S 41: $^1$H - $^{13}$C HMBC NMR spectrum (126 MHz, CDCl$_3$, 25°C) of MTC$^{\text{Na}}·0.75$THF.
**Reaction between MTC\(^{\text{Na}}\) and BO in presence of CS\(_2\):** In an oven dried J. Youngs NMR Tube MTC-0.75THF (50.3 mg, 0.16 mmol, 1 eq.) dissolved in d\(_8\)-THF (0.4 mL) and CS\(_2\) (0.4 mL, 6.6 mmol, 42 equiv.) and BO (7.0 µL, 0.08 mmol, 0.5 equiv.) was added. The mixture was let react for 16 h and analysed by NMR.

**Figure S 42:** \(^1\)H NMR spectrum (400 MHz, d\(_8\)-THF, 25°C) of product mixture from the stochiometric reaction of

$$
\text{MTC·0.75THF + CS}_2 + \text{BO} \rightarrow \text{Product mixture}
$$

**Synthesis of MTC\(^{\text{K}}\):** Inside an Argon filled glovebox, phtalic thioanhydride (164.2 mg, 1.00 mmol) and KO\(^{\text{tBu}}\) (112.2 mg, 1.00 mmol) were loaded into an oven-dried Schkenk fask, brought outside the glovebox and connected to an Schlenkline. Dry THF (25mL) was added and the mixture was stirred overnight giving an orange suspension. All volatiles were removed in vacuum yielding MTC\(^{\text{K}}\) as a orange solid (262.6 mg, 0.95 mmol, 95%). XRD quality crystals were grown by layering a crude reaction mixture with Pentane.

\(\text{H NMR (400 MHz, d}_8\text{-THF, 25°C): } \delta(\text{ppm}): \delta 7.79 \text{ (ddd, } J = 7.7, 1.2, 0.6 \text{ Hz, 1H, } H^1), 7.27 \text{ (ddd, } J = 7.7, 6.4, 2.3 \text{ Hz, 1H, } H^2), 7.23 - 7.15 \text{ (m, 2H, } H^3/4), 1.46 \text{ (s, 9H, } t\text{Bu}).

Due to the insolubility of MTC\(^{\text{K}}\), \(^{13}\)C data was obtained via \(^1\)H-\(^{13}\)C HMBC NMR spectroscopy.
$^{13}\text{C}$($^1\text{H}$) NMR (101 MHz, $d_6$-THF, 25°C); $\delta$(ppm): 208.10 (C1), 169.31 (C8), 148.84 (C2), 131.10 (C7), 129.24 (C6), 129.00 (C4), 127.23 (C5), 126.96 (C2), 81.50 (C9), 28.90 (C10)

FTIR [cm$^{-1}$]: 1684.5 (Ester C=O), 1451.9 (Thiocarboxylate C=O)

HRESI-MS (negative mode): m/z = calculated [M - K]: 237.0585. Found 237.0572

Figure S 43: $^1\text{H}$ NMR spectrum (400 MHz, $d_6$-DMSO, 25°C) of MTC$^K$. 
Section S6: Switchable Catalysis.

εDL ROP protocol: In an argon-filled glovebox, LiHMDS (6.4 mg, 38.5 µmol, 1 equiv.) was dissolved in butylene oxide (1670.0 µl, 1386.9 mg, 19.2 mmol, 500 equiv.) and benzylalcohol (4.0 µl, 4.2 mg, 36.5 µmol, 1 equiv.) was added. The resulting mixture was stirred for 1 min and afterwards ε-decalactone (εDL) (630.6 µl, 655.5 mg, 3.9 mmol, 100 equiv.) was added. Aliquots were removed at regular time intervals and quenched by addition into CDCl$_3$ containing benzoic acid (10 mg/ml) which were then analysed by $^1$H NMR and SEC.

Figure S 45: εDL conversion to PDL polymer versus time plot.
**Figure S 46:** Logarithmic εDL conversion to PDL polymer versus time plot.

**Figure S 47:** Plot showing the development of $M_n$ and polydispersity of PDL with respect to εDL conversion.
**Figure S 48:** Correlation of measured and theoretical $M_n$ of PDL.

**εDL ROP into PTA/CS$_2$/BO ROTERP switch protocol:** In an argon-filled glovebox, LiHMDS (6.4 mg, 38.5 µmol, 1 equiv.) was dissolved in butylene oxide (835.0 µl, 693.5 mg, 9.6 mmol, 250 equiv.) and benzylalcohol (4.0 µl, 4.2 mg, 36.5 µmol, 1 equiv.) was added. The resulting mixture was stirred for 1 min and afterwards ε-decalactone (εDL) (335.3 µl, 327.3 mg, 19.25 mmol, 50 equiv.) was added and ROP was allowed to occur for 15 min. Afterwards CS$_2$ (1083.0 µl, 1364.6 mg, 19.3 mmol) and PTA (442.4 mg, 27.0 mmol, 70 equiv.) were added causing an immediate yellow discolouration of the mixture which was then allowed to react for 30 min at 80°C. The polymer was isolated by two consecutive precipitations from DCM/MeOH, followed by isolation by filtration and drying in a vacuum oven set to 60°C overnight.

**Figure S 49:** Schematic showing εDL ROP to PTA/CS$_2$/BO ROTERP switchable catalysis.
**Figure S 50a:** $^1$H NMR spectra (400 MHz, CDCl$_3$, 25°C) of aliquots removed before and after ROTERP phase of switchable catalysis showing that no further ROP occurs after ROTERP initiation.

**Figure S 51b:** $^1$H NMR spectra (400 MHz, CDCl$_3$, 25°C) of aliquots removed throughout ROP and ROTERP phase of switchable catalysis.
Figure S 52c: Conversion versus time plot (by integration of the $^1$H NMR spectra) of switchable catalysis corresponding to Figure S 50b. Note that aliquot removal in the ROP phase results in the final BO conversion deviating from theoretical 40%.

Figure S 53: $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25°C) of $\varepsilon$DL ROP to PTA/CS$_2$/BO ROTERP polymer. CH$_x$ labels refer to protons adjacent to heteroatoms.
Figure S 54: $^{13}$C{H} NMR spectrum (126 MHz, CDCl$_3$, 25°C) of εDL ROP to PTA/CS$_2$/BO ROTERP polymer.

Figure S 55: Zoom into the Carbonyl region of the $^{13}$C{H} NMR spectrum (126 MHz, CDCl$_3$, 25°C) of εDL ROP to PTA/CS$_2$/BO ROTERP polymer.
Figure S 56: $^1$H - $^{13}$C HMBC NMR spectrum (126 MHz, CDCl$_3$, 25°C) of $\varepsilon$DL ROP to PTA/CS$_2$/BO ROTERP polymer.

Figure S 57: $^{31}$P($^1$H) NMR (162 MHz, CDCl$_3$, 25°C) end-group analysis before and after mechanistic switch.
**Figure S 58**: UV-Vis spectrum of aliquot removed directly after addition of CS$_2$ and PTA (diluted with appropriate BO/CS$_2$ mixture by a factor of 10 prior to measurement).

**Figure S 59**: Overlayed $^7$Li NMR spectra (194 MHz, d$_6$-Acetone capillary, 25°C) at different stages of switchable catalysis. ROCOP refers to adding CS$_2$ alone without PTA.

**Figure S 60**: Reaction colour at different stages of switchable catalysis.
Section S7: Degradation Experiments

**UV degradation**: The respective polymer (50 mg) was dissolved in CDCl$_3$ (0.75 mL) and irradiated for 16h by a broadband Hg UV 1000W UV lamp inside a J. Youngs NMR tube. Afterwards the sample was analysed by $^1$H NMR spectroscopy and SEC.

![NMR Spectra and SEC Traces]

**Figure S 61**: $^1$H NMR spectra (400 MHz, CDCl$_3$, 25°C) phtalic anhydride/PO copolymer before and after irradiation with UV-light.

**Figure S 62**: Overlayed SEC traces of phtalic anhydride/PO copolymer before and after irradiation with UV-light.
**Figure S 63:** $^1$H NMR spectra (400 MHz, CDCl$_3$, 25°C) terpolymer (top) before and (bottom) after irradiation with UV-light.

**Figure S 64:** Overlayed SEC traces before and after UV irradiation of terpolymer before (black) and after (red) irradiation with UV-light.
Oxidative degradation: The respective polymer (50mg) was dispersed in aqueous H$_2$O$_2$ (3 mL) and stirred for 5d in a glass vial. In case of the polyester, all polymer remained dispersed and SEC as well as NMR remained unchanged. In case of the ROTERP polymer the initial yellow suspension gradually turned into a colourless solution with minor amounts of a colourless precipitate. The suspension was extracted with CDCl$_3$, dried over MgSO$_4$, filtered and analysed by NMR and SEC.

Figure S 65: Overlaid SEC traces of phtalic anhydride/PO copolymer before and after dispersion in H$_2$O$_2$. NMR spectra remains unchanged.

Figure S 66: $^1$H NMR spectra (400 MHz, CDCl$_3$, 25°C) of terpolymer (top) before and (bottom) after oxidative degradation. No polymeric material could be detected by SEC.
Section S8: Crystallography

X-Ray data were collected on a BRUKER D8 Venture system. Data were collected at 100(2) K using graphite-monochromated Mo Kα radiation (\(\lambda_\alpha = 0.71073 \, \text{Å}\)). The strategy for the data collection was evaluated by using the Smart software. The data were collected by the standard \(\psi-\omega\) scan techniques and were scaled and reduced using Saint+software. The structures were solved by using Olex2,[3] the structure was solved with the XT[4] structure solution program using Intrinsic Phasing and refined with the XL refinement package[5,6] using Least Squares minimization. Deposition number CCDC 2151056, contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

| Compound | MTC |
|----------|-----|
| **Empirical formula** | \(\text{C}_{40}\text{H}_{58}\text{Li}_2\text{O}_{10}\text{S}_2\) |
| **Formula weight** | 776.86 |
| **Temperature/K** | 100 |
| **Crystal system** | monoclinic |
| **Space group** | \(\text{P}2_1/\text{n}\) |
| **a/Å** | 11.2936(6) |
| **b/Å** | 21.8827(10) |
| **c/Å** | 17.1083(7) |
| **α/°** | 90 |
| **β/°** | 94.544(2) |
| **γ/°** | 90 |
| **Volume/Å\(^3\)** | 4214.8(3) |
| **Z** | 4 |
| **\(\rho_{\text{calc}}\)/\text{g/cm}^3** | 1.224 |
| **μ/mm\(^{-1}\)** | 0.179 |
| **F(000)** | 1664.0 |
| **Crystal size/mm\(^3\)** | 0.6 × 0.16 × 0.15 |
| **Crystal shape** | needle |
| **Radiation** | MoKα (\(\lambda = 0.71073\)) |
| 2θ range for data collection/° | 4.068 to 50.842 |
|-------------------------------|-----------------|
| Index ranges                  | -13 ≤ h ≤ 13, 0 ≤ k ≤ 26, 0 ≤ l ≤ 20 |
| Reflections collected         | 7771            |
| Independent reflections       | 7771 [R_{int} = 0.0, R_{sigma} = 0.0235] |
| Data/restraints/parameters    | 7771/0/604      |
| Goodness-of-fit on F^2        | 1.116           |
| Final R indexes [I>=2σ (I)]   | R_1 = 0.0472, wR_2 = 0.0929 |
| Final R indexes [all data]    | R_1 = 0.0561, wR_2 = 0.0967 |
| Largest diff. peak/hole / e Å^-3 | 0.26/-0.24 |

| Compound                        | MTC^Na          | MTC^K           |
|----------------------------------|-----------------|-----------------|
| Empirical formula                | C_{12}H_{13}NaO_{3}S | C_{96}H_{104}K_{8}O_{24}S_{8} |
| Formula weight                   | 260.27          | 2211.07         |
| Temperature/K                    | 100             | 100             |
| Crystal system                   | triclinic       | monoclinic      |
| Space group                      | P-1             | P2/n            |
| a/Å                              | 5.9833(6)       | 15.1783(13)     |
| b/Å                              | 9.3642(10)      | 6.6961(6)       |
| c/Å                              | 11.7461(12)     | 30.176(3)       |
| α/°                              | 90.127(4)       | 90              |
| β/°                              | 101.890(4)      | 104.412(3)      |
| γ/°                              | 97.726(4)       | 90              |
| Volume/Å³                        | 637.85(11)      | 2970.4(5)       |
| Z                                | 2               | 1               |
| ρ_{calc}/g/cm³                   | 1.355           | 1.236           |
| μ/mm⁻¹                           | 0.280           | 0.492           |
| F(000)                           | 272.0           | 1152.0          |
| Crystal size/mm³                 | 0.24 × 0.24 × 0.11 | 0.5 × 0.14 × 0.1 |
| Crystal shape                    | Colorless       | colorless       |
| Crystal color       | needle       | needle       |
|---------------------|--------------|--------------|
| ion                 | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 4.392 to 53.054 | 4.18 to 50.904 |
| Index ranges        | -7 ≤ h ≤ 7, -11 ≤ k ≤ 11, 0 ≤ l ≤ 14 | -18 ≤ h ≤ 18, -8 ≤ k ≤ 8, -36 ≤ l ≤ 36 |
| Reflections collected | 2612         | 48719        |
| Independent reflections | 2612 [R_int = 0.0, R_sigma = 0.0314] | 5700 [R_int = 0.1002, R_sigma = 0.0441] |
| Data/restraints/parameters | 2612/0/157   | 5700/0/314   |
| Goodness-of-fit on F² | 1.054        | 1.150        |
| Final R indexes [I≥2σ (I)] | R₁ = 0.0533, wR₂ = 0.1478 | R₁ = 0.0819, wR₂ = 0.2408 |
| Final R indexes [all data] | R₁ = 0.0598, wR₂ = 0.1521 | R₁ = 0.0829, wR₂ = 0.2420 |
| Largest diff. peak/hole / e Å³ | 0.48/-0.46 | 1.85/-0.64 |
Section S9: Bibliography

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