Triptycene End-Capped Benzothienobenzothiophene and Naphthothienobenzothiophene

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1 NMR Spectra

1.1 1D-\(^1\)H and \(^{13}\)C NMR Spectra

Figure S1. \(^1\)H NMR spectrum (300 MHz, CDCl\(_3\)) of 3.

Figure S2. \(^{13}\)C NMR spectrum (50 MHz, CDCl\(_3\)) of 3.
Figure S3. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 5a.

Figure S4. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 5a.
Figure S5. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of T-BTBT.

Figure S6. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of T-BTBT.
Figure S7. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4b.

Figure S8. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4b.
Figure S9. $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 5b.

Figure S10. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 5b.
Figure S11. $^1$H NMR spectrum (300 MHz, CDCl$_3$) of T-NTBT.

Figure S12. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of T-NTBT.
1.2 2D-NMR Spectra

Figure S13. HSQC spectrum of 3.

Figure S14. HMBC spectrum of 3.
Figure S15. HSQC spectrum of 5a.

Figure S16. HMBC spectrum of 5a.
Figure S17. H,H-COSY spectrum of 5a.

Figure S18. HSQC spectrum of T-BTBT.
Figure S19. HMBC spectrum of T-BTBT.

Figure 20. H,H-COSY spectrum of T-BTBT.
Figure S21. HSQC spectrum of 4b.

Figure S22. HMBC spectrum of 4b.
Figure S23. HSQC spectrum of 5b.

Figure S24. HMBC spectrum of 5b.
Figure S25. HSQC spectrum of T-NTBT.

Figure S26. HMBC spectrum of T-NTBT.
2 FT-IR Spectra

Figure S27. IR spectrum (ATR) of 3.

Figure S28. IR spectrum (ATR) of 4a.
Figure S29. IR spectrum (ATR) of BTTBT.

Figure S30. IR spectrum (ATR) of 4b.
Figure S31. IR spectrum (ATR) of 5b.

Figure S32. IR spectrum (ATR) of BTTBT.
3 Mass Spectra

**Figure S33.** HRMS spectrum (El+) of 3.

**Figure S34.** HRMS spectrum (DART) of 5a.
Figure S35. HRMS spectrum (DART) of T-BTBT.

Figure S36. HRMS spectrum (EI+) of 4b.
Figure S37. HRMS spectrum (EI+) of 5b.

Figure S38. HRMS (DART) of T-NTBT.
4 Side Products During T-NTBT Formation

The reaction from alkyne 5b to T-NTBT gave the desired product only in 6% yield (see Scheme 1 in the main document). To investigate the reason for this low yield, an aliquot of the crude product after column chromatography (PE:CHCl₃ = 3:1; Rₚ = 0.33) was purified via recycling HPLC (SiO₂, n-hexane:CHCl₃ = 3:1, 20 mL/min) to identify side products. Despite showing only a single spot on the TLC three main fractions could be isolated. It should be noted, that T-NTBT did hardly dissolve in the eluent mixture and any remaining solid was filtered off prior to injection onto the HPLC. Hence, it could not be identified in the chromatogram and the relative intensities of the fractions do not give any information about ratio between side products and T-NTBT. The three fractions were analyzed via ¹H NMR spectroscopy and mass spectrometry (see spectra below). Due to the small sample amount no full characterization could be performed. However, the data revealed that one-fold cyclization products and hydrodebrominated products are formed. Since those products cannot be separated by column chromatography, it is reasonable that the yield of T-NTBT is further reduced due to the additional recrystallization step.

Figure S39. Recycling HPLC chromatogram (SiO₂, n-hexane:CHCl₃ = 3:1, 20 mL/min) of the crude T-NTBT product.
Figure S40. $^1$H-NMR spectrum (CDCl$_3$, 300 MHz) of fraction A.

Figure S41. HRMS (DART) of fraction A.
Figure S42. $^1$H-NMR spectrum (CDCl$_3$, 300 MHz) of fraction B.

Figure S43. HRMS (DART) of fraction B.
Figure S44. $^1$H-NMR spectrum (CDCl$_3$, 300 MHz) of fraction C.
Figure S45. HRMS (DART) of fraction C.

5 Crystal Structure Analysis

5.1 Crystal Structures of T-BTBT

Figure S46. Crystal structures of T-BTBT. a,b,e) asymmetric unit. c,f) packing. Asymmetric unit highlighted in red. Triptycene units and solvent molecules omitted for clarity.
5.2 Definition of π-π-Distances

For the determination of face-to-face π-π-distances between two π stacked molecules a centroid was generated from all atoms of the aromatic backbone in Mercury. The distance from this centroid to the plane containing all atoms of the aromatic backbone of the adjacent molecule was then used as the π-π distance. The distance of edge-to-face π stacked molecules was determined as the shortest C⋯H distance.

Figure S47. Determination of π-π-distances: a) atoms used for centroid and plane generation. b) distance between a centroid and a plane of two adjacent π stacked T-BTBT molecules.

5.3 T-BTBT Polymorphs by Physical Vapor Transport

Figure S48. Microscopic Images of crystals of T-BTBT generated by physical vapour transport in an Ar stream at 280 °C:[S1] a) polymorph δ2 (monoclinic, C2/c), b) polymorph δ1 (orthorhombic, Pca21).

5.4 Crystal Data

Figure S49. Thermal atomic displacement ellipsoid plot of the asymmetric unit of 3. The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.
Table S1. Crystal data and structure refinement for 3.

| Property                                | Value                        |
|-----------------------------------------|------------------------------|
| Empirical formula                       | C_{20}H_{12}BrI              |
| Formula weight                          | 459.11                       |
| Temperature                             | 200(2) K                     |
| Wavelength                              | 0.71073 Å                    |
| Crystal system                          | orthorhombic                 |
| Space group                             | Pbca                         |
| Z                                       | 8                            |
| Unit cell dimensions                    |                              |
| a = 12.3936(6) Å                       | \( \alpha = 90 \) deg.      |
| b = 9.1769(4) Å                        | \( \beta = 90 \) deg.       |
| c = 28.4348(13) Å                      | \( \gamma = 90 \) deg.      |
| Volume                                  | 3234.0(3) Å³                 |
| Density (calculated)                    | 1.89 g/cm³                   |
| Absorption coefficient                  | 4.45 mm⁻¹                    |
| Crystal shape                           | brick                        |
| Crystal size                            | 0.299 x 0.242 x 0.219 mm³    |
| Crystal colour                          | colourless                   |
| Theta range for data collection         | 1.4 to 25.0 deg.             |
| Index ranges                            | -14 \leq h \leq 14, -10 \leq k \leq 10, -33 \leq l \leq 33 |
| Reflections collected                   | 18811                        |
| Independent reflections                 | 2863 (R(int) = 0.0296)       |
| Observed reflections                    | 2724 (I > 2\sigma(I))       |
| Absorption correction                   | Semi-empirical from equivalents |
| Max. and min. transmission              | 0.49 and 0.40                |
| Refinement method                       | Full-matrix least-squares on F² |
| Data/restraints/parameters              | 2863 / 14 / 218              |
| Goodness-of-fit on F²                   | 1.33                         |
| Final R indices (I>2\sigma(I))          | R1 = 0.026, wR2 = 0.065      |
| Largest diff. peak and hole             | 0.29 and -0.46 eÅ⁻³          |

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å²) for 3. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| Atom | x     | y     | z     | U_{eq} |
|------|-------|-------|-------|--------|
| I1   | 0.5389(2) | 0.3888(2) | 0.8202(1) | 0.0366(2) |
| Br1  | 0.7605(4) | 0.1761(6) | 0.7802(2) | 0.0349(7)  |
| Br1B | 0.5277(9) | 0.3777(10) | 0.8141(3) | 0.062(3)   |
| I1B  | 0.7612(7) | 0.1744(10) | 0.7874(4) | 0.0331(11) |
| C1   | 0.6205(3) | 0.2626(4) | 0.6032(1) | 0.0208(7)  |
| H1   | 0.6850   | 0.2039  | 0.5938  | 0.025      |
| C2   | 0.4533(3) | 0.4155(4) | 0.6278(1) | 0.0215(7)  |
| H2   | 0.3890   | 0.4743  | 0.6373  | 0.026      |
| C11  | 0.6144(3) | 0.2907(4) | 0.6558(1) | 0.0206(7)  |
| C12  | 0.6838(3) | 0.2358(4) | 0.6894(1) | 0.0237(7)  |
| H12  | 0.7452   | 0.1804  | 0.6804  | 0.028      |
| C13  | 0.6625(3) | 0.2630(4) | 0.7368(1) | 0.0256(8)  |
| C14  | 0.5741(3) | 0.3448(4) | 0.7498(1) | 0.0260(8)  |
| C15  | 0.5050(3) | 0.4021(4) | 0.7159(1) | 0.0243(7)  |
| H15  | 0.4449   | 0.4602  | 0.7249  | 0.029      |
| C16  | 0.5251(3) | 0.3731(4) | 0.6692(1) | 0.0204(7)  |
| C21  | 0.5140(3) | 0.1899(4) | 0.5905(1) | 0.0199(7)  |
| C22  | 0.5011(3) | 0.0590(4) | 0.5677(1) | 0.0223(7)  |
| H22  | 0.5622   | 0.0029  | 0.5589  | 0.027      |
| C23  | 0.3974(3) | 0.0093(4) | 0.5578(1) | 0.0257(8)  |
| H23  | 0.3879   | -0.0803 | 0.5416  | 0.031      |
| C24  | 0.3083(3) | 0.0897(4) | 0.5713(1) | 0.0235(7)  |
| H24  | 0.2379   | 0.0545  | 0.5645  | 0.028      |
| C25  | 0.3208(3) | 0.2215(4) | 0.5946(1) | 0.0215(7)  |
Table S3. Crystal data and structure refinement for 4a.

| Property                        | Value                  |
|---------------------------------|------------------------|
| Empirical formula               | C_{28.50}H_{16.50}Br_{2}Cl_{1.50} |
| Formula weight                  | 571.91                 |
| Temperature                     | 200(2) K               |
| Wavelength                      | 0.71073 Å              |
| Crystal system                  | monoclinic             |
| Space group                     | C2/c                   |
| Z                               | 8                      |
| Unit cell dimensions            | a = 29.1864(10) Å, α = 90 deg. |
|                                | b = 9.0090(3) Å, β = 116.7172(8) deg. |
|                                | c = 19.5948(7) Å, γ = 90 deg. |
| Volume                          | 4602.2(3) Å^3          |
| Density (calculated)            | 1.65 g/cm^3            |
| Absorption coefficient          | 3.71 mm^-1             |
| Crystal shape                   | brick                  |
| Crystal size                    | 0.278 x 0.235 x 0.226 mm^3 |
| Crystal colour                  | colourless             |
| Theta range for data collection | 1.6 to 25.0 deg.       |
| Index ranges                    | -34≤h≤32, -10≤k≤10, -23≤l≤23 |
| Reflections collected           | 21491                  |
| Independent reflections         | 4075 (R(int) = 0.0231)  |
| Observed reflections            | 3525 (I > 2σ(I))       |
| Absorption correction           | Semi-empirical from equivalents |
| Max. and min. transmission      | 0.50 and 0.44          |
| Refinement method               | Full-matrix least-squares on F^2 |
| Data/restraints/parameters      | 4075 / 24 / 307        |
| Goodness-of-fit on F^2          | 1.04                   |
| Final R indices (I>2σ(I))       | R1 = 0.028, wR2 = 0.069 |
| Largest diff. peak and hole     | 0.68 and -0.63 eÅ^3    |
Table S4. Atomic coordinates and equivalent isotropic displacement parameters (Å²) for 4a. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| Atom | x    | y    | z    | U_{eq} |
|------|------|------|------|--------|
| Br1  | 0.1861(1) | 0.3624(1) | 0.6400(1) | 0.0443(1) |
| Br2  | 0.1251(1) | 0.1875(1) | 0.4219(1) | 0.0511(1) |
| C1   | 0.3667(1) | 0.3902(3) | 0.8977(1) | 0.0296(6) |
| H1   | 0.3490    | 0.4612    | 0.9172    | 0.036    |
| C2   | 0.4125(1) | 0.2059(3) | 0.8466(2) | 0.0304(6) |
| H2   | 0.4302    | 0.1350    | 0.8270    | 0.036    |
| C11  | 0.3322(1) | 0.3342(3) | 0.8171(1) | 0.0276(5) |
| C12  | 0.2815(1) | 0.3726(3) | 0.7722(1) | 0.0290(5) |
| H12  | 0.2647    | 0.4414    | 0.7902    | 0.035    |
| C13  | 0.2557(1) | 0.3084(3) | 0.7006(1) | 0.0296(6) |
| C14  | 0.2790(1) | 0.2080(3) | 0.6720(1) | 0.0294(6) |
| C15  | 0.3310(1) | 0.1716(3) | 0.7190(2) | 0.0297(6) |
| H15  | 0.3480    | 0.1031    | 0.7014    | 0.036    |
| C16  | 0.3568(1) | 0.2345(3) | 0.7898(1) | 0.0274(5) |
| C17  | 0.2533(1) | 0.1417(3) | 0.5976(2) | 0.0318(6) |
| C18  | 0.2348(1) | 0.0850(3) | 0.5363(2) | 0.0322(6) |
| C21  | 0.2145(1) | 0.0132(3) | 0.4631(1) | 0.0318(6) |
| C22  | 0.1658(1) | 0.0430(3) | 0.4052(2) | 0.0339(6) |
| C23  | 0.1467(1) | -0.0287(4)| 0.3354(2) | 0.0474(8) |
| H23  | 0.1132    | -0.0072   | 0.2967    | 0.057    |
| C24  | 0.1770(2) | -0.1316(4)| 0.3229(2) | 0.0629(10)|
| H24  | 0.1642    | -0.1820   | 0.2753    | 0.075    |
| C25  | 0.2256(2) | -0.1618(4)| 0.3790(2) | 0.0658(11)|
| H25  | 0.2463    | -0.2325   | 0.3697    | 0.079    |
| C26  | 0.2446(1) | -0.0908(4)| 0.4485(2) | 0.0500(8) |
| H26  | 0.2783    | -0.1123   | 0.4867    | 0.060    |
| C31  | 0.3857(1) | 0.2499(3) | 0.9465(1) | 0.0306(6) |
| C32  | 0.3809(1) | 0.2167(3) | 1.0117(2) | 0.0375(6) |
| H32  | 0.3637    | 0.2827    | 1.0303    | 0.045    |
| C33  | 0.4019(1) | 0.0839(4) | 1.0498(2) | 0.0463(8) |
| H33  | 0.3984    | 0.0588    | 1.0944    | 0.056    |
| C34  | 0.4275(1) | -0.0106(3)| 1.0239(2) | 0.0465(8) |
| H34  | 0.4422    | -0.0991   | 1.0514    | 0.056    |
| C35  | 0.4319(1) | 0.0217(3) | 0.9579(2) | 0.0369(6) |
| H35  | 0.4492    | -0.0448   | 0.9396    | 0.044    |
| C36  | 0.4109(1) | 0.1522(3) | 0.9190(1) | 0.0304(6) |
| C41  | 0.4141(1) | 0.4563(3) | 0.8951(1) | 0.0294(6) |
| C42  | 0.4346(1) | 0.5957(3) | 0.9206(2) | 0.0367(6) |
| H42  | 0.4178    | 0.6635    | 0.9391    | 0.044    |
| C43  | 0.4799(1) | 0.6347(3) | 0.9186(2) | 0.0434(7) |
| H43  | 0.4946    | 0.7295    | 0.9368    | 0.052    |
| C44  | 0.5039(1) | 0.5378(3) | 0.8907(2) | 0.0430(7) |
| H44  | 0.5348    | 0.5667    | 0.8892    | 0.052    |
| C45  | 0.4833(1) | 0.3978(3) | 0.8646(2) | 0.0378(6) |
| H45  | 0.4998    | 0.3310    | 0.8453    | 0.045    |
| C46  | 0.4385(1) | 0.3575(3) | 0.8673(1) | 0.0306(6) |
| C51  | 0.4920(3) | 0.1078(7) | 1.2794(4) | 0.0563(17)|
| H51  | 0.5100    | 0.1121    | 1.3365    | 0.068    |
| Cl1  | 0.5230(2) | 0.2247(3) | 1.2439(2) | 0.1228(12)|
| Cl2  | 0.4276(1) | 0.1526(3) | 1.2486(1) | 0.0865(7) |
| Cl3  | 0.4971(5) | -0.0760(2)| 1.2499(9) | 0.0860(12)|
Figure S51. Thermal atomic displacement ellipsoid plot of the asymmetric unit of T-BTBT (α). The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

Table S5. Crystal data and structure refinement for T-BTBT (α).

|                           |                                                                 |
|---------------------------|-----------------------------------------------------------------|
| Empirical formula         | \(\text{C}_{28.50}\text{H}_{16.50}\text{Cl}_{1.50}\text{S}_{2}\) |
| Formula weight            | 476.21                                                          |
| Temperature               | 200(2) K                                                        |
| Wavelength                | 0.71073 Å                                                       |
| Crystal system            | orthorhombic                                                    |
| Space group               | \(\text{P}2_1\text{\,2_1\,2_1}\)                               |
| Z                         | 8                                                               |
| Unit cell dimensions      | \(a = 8.5854(3) \text{ Å}, \alpha = 90 \text{ deg.}\)          |
|                           | \(b = 11.9816(4) \text{ Å}, \beta = 90 \text{ deg.}\)          |
|                           | \(c = 43.0026(15) \text{ Å}, \gamma = 90 \text{ deg.}\)        |
| Volume                    | 4423.5(3) Å                                                     |
| Density (calculated)      | 1.43 g/cm\(^3\)                                                 |
| Absorption coefficient    | 0.44 mm\(^1\)                                                   |
| Crystal shape             | plate                                                           |
| Crystal size              | 0.167 x 0.136 x 0.026 mm\(^3\)                                  |
| Crystal colour            | colourless                                                      |
| Theta range for data collection | 1.8 to 25.7 deg.                                              |
| Index ranges              | -10 \(\leq\) h \leq 10, -14 \(\leq\) k \leq 14, -52 \(\leq\) l \leq 52 |
| Reflections collected     | 44024                                                           |
| Independent reflections   | 8424 (\(R(\text{int}) = 0.0457\))                               |
| Observed reflections      | 7537 (I > 2\(\sigma(I)\))                                      |
| Absorption correction     | Semi-empirical from equivalents                                |
| Max. and min. transmission| 0.96 and 0.89                                                   |
| Refinement method         | Full-matrix least-squares on \(F^2\)                           |
| Data/restraints/parameters| 8424 / 1332 / 642                                                |
| Goodness-of-fit on \(F^2\) | 1.05                                                            |
| Final R indices (I>2\(\sigma(I)\)) | R1 = 0.041, wR2 = 0.094                                       |
| Absolute structure parameter | 0.00(2)                                                        |
| Largest diff. peak and hole | 0.39 and -0.48 eÅ\(^3\)                                       |

Table S6. Atomic coordinates and equivalent isotropic displacement parameters (Å\(^2\)) for T-BTBT (α). 
\(U_{eq}\) is defined as one third of the trace of the orthogonalized \(U_{ij}\) tensor.

| Atom | x       | y       | z       | \(U_{eq}\) |
|------|---------|---------|---------|------------|
| S11  | 0.2203(1)| 0.0901(1)| 0.2627(1)| 0.0259(2)  |
| S21  | 0.5289(1)| -0.1804(1)| 0.2609(1)| 0.0281(2)  |
| C11  | -0.0290(5)| -0.0098(3)| 0.3738(1)| 0.0270(9)  |
| H11  | -0.1009 | 0.0553  | 0.3713  | 0.032      |
| C21  | 0.1580(5)| -0.1789(3)| 0.3801(1)| 0.0273(9)  |
| H21  | 0.2295 | -0.2442 | 0.3826  | 0.033      |
| C111 | -0.1131(5)| -0.1220(3)| 0.3729(1)| 0.0260(8)  |
|   | C121 | 0.2716(5) | -0.1380(4) | 0.3690(1) | 0.0321(10) |
|---|------|-----------|------------|-----------|-------------|
| H121 | 0.3398 | -0.0762 | 0.3665 | 0.039 |
| C131 | 0.3289(5) | -0.2470(4) | 0.3687(1) | 0.0380(11) |
| H131 | 0.4375 | -0.2592 | 0.3661 | 0.046 |
| C141 | 0.2316(5) | -0.3370(4) | 0.3722(1) | 0.0352(10) |
| H141 | 0.2728 | -0.4105 | 0.3718 | 0.042 |
| C151 | 0.0713(5) | -0.3203(4) | 0.3762(1) | 0.0312(9) |
| H151 | 0.0033 | -0.3822 | 0.3787 | 0.037 |
| C161 | 0.0133(5) | -0.2126(3) | 0.3765(1) | 0.0264(9) |
| C211 | 0.0582(5) | -0.0095(3) | 0.4048(1) | 0.0312(9) |
| C221 | 0.0332(6) | 0.0630(4) | 0.4291(1) | 0.0366(10) |
| H221 | 0.0392 | 0.1226 | 0.4272 | 0.044 |
| C231 | 0.1165(6) | 0.0472(4) | 0.4567(1) | 0.0462(12) |
| H231 | 0.1018 | 0.0970 | 0.4737 | 0.055 |
| C241 | 0.2186(6) | -0.0393(4) | 0.4595(1) | 0.0461(12) |
| H241 | 0.2751 | -0.0486 | 0.4783 | 0.055 |
| C251 | 0.2414(5) | -0.1142(4) | 0.4352(1) | 0.0396(11) |
| H251 | 0.3127 | -0.1744 | 0.4374 | 0.048 |
| C261 | 0.1596(5) | -0.1004(4) | 0.4078(1) | 0.0302(9) |
| C311 | 0.0930(5) | -0.0169(3) | 0.3480(1) | 0.0259(9) |
| C321 | 0.0985(5) | 0.0510(3) | 0.3222(1) | 0.0250(9) |
| H321 | 0.0327 | 0.1143 | 0.3203 | 0.030 |
| C331 | 0.2046(5) | 0.0231(3) | 0.2988(1) | 0.0238(8) |
| C341 | 0.3038(4) | -0.0702(3) | 0.3012(1) | 0.0230(8) |
| C351 | 0.2985(5) | -0.1360(3) | 0.3282(1) | 0.0259(9) |
| H351 | 0.3666 | -0.1978 | 0.3306 | 0.031 |
| C361 | 0.1932(4) | -0.1094(3) | 0.3510(1) | 0.0255(9) |
| C371 | 0.3917(4) | -0.0838(3) | 0.2729(1) | 0.0226(8) |
| C381 | 0.3599(4) | -0.0049(3) | 0.2509(1) | 0.0231(8) |
| C411 | 0.4458(4) | -0.0188(3) | 0.2225(1) | 0.0242(8) |
| C421 | 0.5445(4) | -0.1131(3) | 0.2246(1) | 0.0257(8) |
| C431 | 0.6374(5) | -0.1450(4) | 0.1999(1) | 0.0333(10) |
| H431 | 0.7020 | -0.2091 | 0.2014 | 0.040 |
| C441 | 0.6344(5) | -0.0818(4) | 0.1730(1) | 0.0357(10) |
| C451 | 0.6800 | -0.1026 | 0.1558 | 0.043 |
| H451 | 0.5392(5) | 0.0119(4) | 0.1708(1) | 0.0343(10) |
| C461 | 0.5399 | 0.0546 | 0.1521 | 0.041 |
| H461 | 0.4438(5) | 0.0442(3) | 0.1950(1) | 0.0300(9) |
| S12 | 0.3782 | 0.1077 | 0.1931 | 0.036 |
| S22 | 0.6378(1) | 0.1088(1) | 0.3007(1) | 0.0270(3) |
| S22 | 0.9548(1) | 0.3732(1) | 0.2935(1) | 0.0267(3) |
| C12 | 0.4609(5) | 0.2118(3) | 0.4171(1) | 0.0322(9) |
| H12 | 0.3863 | 0.1477 | 0.4166 | 0.039 |
| C22 | 0.6541(5) | 0.3784(3) | 0.4196(1) | 0.0308(9) |
| H22 | 0.7287 | 0.4424 | 0.4204 | 0.037 |
| C112 | 0.5776(5) | 0.2038(3) | 0.4439(1) | 0.0302(9) |
| C122 | 0.5864(6) | 0.1192(4) | 0.4657(1) | 0.0398(11) |
| H122 | 0.5177 | 0.0571 | 0.4647 | 0.048 |
| C132 | 0.6973(6) | 0.1265(4) | 0.4892(1) | 0.0484(13) |
| H132 | 0.7045 | 0.0685 | 0.5042 | 0.058 |
| C142 | 0.7957(6) | 0.2153(4) | 0.4911(1) | 0.0462(12) |
| H142 | 0.8696 | 0.2193 | 0.5075 | 0.055 |
| C152 | 0.7887(6) | 0.3006(4) | 0.4690(1) | 0.0388(11) |
| H152 | 0.8584 | 0.3621 | 0.4701 | 0.047 |
| C162 | 0.6789(5) | 0.2946(3) | 0.4456(1) | 0.0297(9) |
| C212 | 0.3796(5) | 0.3245(3) | 0.4202(1) | 0.0297(9) |
| C222 | 0.2206(5) | 0.3429(4) | 0.4207(1) | 0.0378(11) |
| H222 | 0.1499 | 0.2819 | 0.4196 | 0.045 |
| C232 | 0.1657(6) | 0.4515(4) | 0.4229(1) | 0.0399(11) |
| H232 | 0.0567 | 0.4650 | 0.4232 | 0.048 |
| C242 | 0.2669(6) | 0.5394(4) | 0.4246(1) | 0.0401(11) |
|         |          |          |          |          |
|---------|----------|----------|----------|----------|
| S1B2    | 0.9448(16) | 0.3879(11) | 0.3153(3) | 0.034(4)  |
| S2B2    | 0.7012(14) | 0.1144(10) | 0.2790(3) | 0.025(3)  |
| C31B2   | 0.692(6)    | 0.345(4)   | 0.3936(9) | 0.021(12) |
| C32B2   | 0.807(5)    | 0.387(3)   | 0.3741(7) | 0.029(10) |
| H32B2   | 0.7875     | 0.1304     | 0.1863    | 0.040     |
| C33B2   | 0.819(5)    | 0.341(4)   | 0.4457(7) | 0.042(11) |
| C34B2   | 0.732(10)   | 0.245(6)   | 0.3355(10)| 0.018(12) |
| C35B2   | 0.625(5)    | 0.199(3)   | 0.3569(8) | 0.028(9)  |
| C41B2   | 0.611(6)    | 0.246(4)   | 0.3860(8) | 0.014(10) |
| C42B2   | 0.611(6)    | 0.246(4)   | 0.3860(8) | 0.014(10) |
| C51     | 0.3589(7)   | 0.7057(5)  | 0.5337(1) | 0.0575(14)|
| H51     | 0.4344      | 0.6608     | 0.5462    | 0.067     |
| Cl1     | 0.1751(2)   | 0.6825(2)  | 0.5493(1) | 0.0935(6) |
| Cl2     | 0.3718(3)   | 0.6595(2)  | 0.4958(1) | 0.0847(6) |
| Cl3     | 0.4136(3)   | 0.8448(2)  | 0.5372(1) | 0.1001(7) |
Figure S52. Thermal atomic displacement ellipsoid plot of the asymmetric unit of T-BTBT (β). The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

Table S7. Crystal data and structure refinement for T-BTBT (β).

| Property                                | Value                                      |
|-----------------------------------------|--------------------------------------------|
| Empirical formula                       | C_{29.50}H_{19}O_{0.50}S_{2}              |
| Formula weight                          | 445.57                                     |
| Temperature                             | 200(2) K                                   |
| Wavelength                              | 1.54178 Å                                  |
| Crystal system                          | orthorhombic                               |
| Space group                             | P2_12_1                                   |
| Z                                       | 8                                          |
| Unit cell dimensions                    | a = 8.6425(7) Å, b = 11.8656(10) Å, c = 42.851(5) Å |
| Volume                                  | 4394.3(7) Å³                              |
| Density (calculated)                    | 1.35 g/cm³                                 |
| Absorption coefficient                  | 2.32 mm⁻¹                                  |
| Crystal shape                           | plate                                      |
| Crystal size                            | 0.120 x 0.087 x 0.018 mm³                  |
| Crystal colour                          | colourless                                 |
| Theta range for data collection         | 4.1 to 55.1 deg.                          |
| Index ranges                            | -9 ≤ h ≤ 5, -12 ≤ k ≤ 12, -41 ≤ l ≤ 45    |
| Reflections collected                   | 8897                                       |
| Independent reflections                 | 4540 (R(int) = 0.1031)                     |
| Observed reflections                    | 2787 (I > 2σ(I))                          |
| Absorption correction                   | Semi-empirical from equivalents            |
| Max. and min. transmission              | 1.50 and 0.59                             |
| Refinement method                       | Full-matrix least-squares on F²           |
| Data/restraints/parameters              | 4540 / 564 / 580                          |
| Goodness-of-fit on F²                   | 1.11                                       |
| Final R indices (I>2σ(I))               | R1 = 0.081, wR2 = 0.141                    |
| Absolute structure parameter            | 0.14(7)                                   |
| Largest diff. peak and hole             | 0.41 and -0.41 eÅ⁻³                       |

Table S8. Atomic coordinates and equivalent isotropic displacement parameters (Å²) for T-BTBT (β). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| Atom  | x       | y       | z       | U_{eq}  |
|-------|---------|---------|---------|---------|
| S11   | 0.7788(5) | 0.3911(3) | 0.7620(1) | 0.0436(11) |
| S21   | 0.4700(5) | 0.6622(3) | 0.7610(1) | 0.0482(12) |
| C11   | 1.029(2)  | 0.4895(13) | 0.8734(4) | 0.047(4)   |
| H11   | 1.1012    | 0.4239   | 0.8712   | 0.057      |
| C21   | 0.8433(18) | 0.6615(13) | 0.8798(4) | 0.041(3)   |
| H21   | 0.7708    | 0.7265   | 0.8826   | 0.049      |
| C111  | 0.948(2)  | 0.4908(13) | 0.9042(4) | 0.047(4)   |
| C121  | 0.969(2)  | 0.4201(14) | 0.9292(4) | 0.057(5)   |
| H121  | 1.0395    | 0.3592   | 0.9273   | 0.069      |
|    |   |   |   |   |
|----|---|---|---|---|
| C131 | 0.892(2) | 0.4338(16) | 0.9568(4) | 0.060(5) |
| H131 | 0.9102   | 0.3837   | 0.9736   | 0.072   |
| C141 | 0.787(2) | 0.5207(16) | 0.9601(4) | 0.060(5) |
| H141 | 0.7307   | 0.5290   | 0.9790   | 0.072   |
| C151 | 0.763(2) | 0.5965(17) | 0.9355(4) | 0.064(5) |
| H151 | 0.6948   | 0.6587   | 0.9377   | 0.077   |
| C161 | 0.8439(19) | 0.5782(13) | 0.9073(4) | 0.046(4) |
| C211 | 0.1139(19) | 0.6025(14) | 0.8724(4) | 0.043(4) |
| C221 | 1.270(2) | 0.6194(15) | 0.8692(4) | 0.053(4) |
| H221 | 1.3382   | 0.5571   | 0.8669   | 0.063   |
| C231 | 1.328(2) | 0.7282(15) | 0.8695(4) | 0.057(5) |
| H231 | 1.4362   | 0.7396   | 0.8673   | 0.068   |
| C241 | 1.234(2) | 0.8190(15) | 0.8727(4) | 0.054(4) |
| H241 | 1.2756   | 0.8930   | 0.8724   | 0.064   |
| C251 | 1.074(2) | 0.8030(14) | 0.8765(4) | 0.048(4) |
| H251 | 1.0082   | 0.8665   | 0.8792   | 0.058   |
| C261 | 1.1014(19) | 0.6958(13) | 0.8764(4) | 0.042(4) |
| C311 | 0.8018(19) | 0.3944(15) | 0.8473(4) | 0.049(4) |
| C321 | 0.9010(19) | 0.4302(14) | 0.8211(4) | 0.046(4) |
| H321 | 0.9670   | 0.3668   | 0.8187   | 0.055   |
| C331 | 0.7945(18) | 0.4590(12) | 0.7977(4) | 0.037(4) |
| C341 | 0.6957(17) | 0.5510(13) | 0.8004(4) | 0.038(4) |
| C351 | 0.7043(18) | 0.6171(13) | 0.8280(4) | 0.041(4) |
| H351 | 0.6380   | 0.6803   | 0.8306   | 0.050   |
| C361 | 0.8090(18) | 0.5894(13) | 0.8511(4) | 0.041(4) |
| C371 | 0.6089(16) | 0.5641(12) | 0.7730(4) | 0.034(4) |
| C381 | 0.6409(19) | 0.4876(13) | 0.7504(4) | 0.040(4) |
| C411 | 0.5542(2) | 0.5019(13) | 0.7223(4) | 0.042(4) |
| C421 | 0.4548(18) | 0.5960(12) | 0.7248(3) | 0.038(4) |
| C431 | 0.3593(17) | 0.6263(14) | 0.7000(4) | 0.042(4) |
| H431 | 0.2924   | 0.6896   | 0.7016   | 0.051   |
| C441 | 0.3632(2) | 0.5625(14) | 0.6729(4) | 0.053(5) |
| H441 | 0.2992   | 0.5842   | 0.6560   | 0.064   |
| C451 | 0.4572(2) | 0.4680(15) | 0.6694(4) | 0.053(4) |
| H451 | 0.4571   | 0.4261   | 0.6505   | 0.063   |
| C461 | 0.5521(18) | 0.4363(13) | 0.6945(3) | 0.040(4) |
| H461 | 0.6152   | 0.3710   | 0.6929   | 0.048   |
| S12  | 0.6341(5) | 0.8721(4) | 0.6997(1) | 0.0553(13) |
| S22  | 0.9518(5) | 0.6064(4) | 0.7049(1) | 0.0522(12) |
| C12  | 0.4532(2) | 0.7741(14) | 0.5826(4) | 0.050(4) |
| H12  | 0.3784   | 0.8385   | 0.5840   | 0.060   |
| C22  | 0.6471(19) | 0.6094(16) | 0.5790(4) | 0.053(4) |
| H22  | 0.7227   | 0.5458   | 0.5777   | 0.064   |
| C112 | 0.5698(19) | 0.7860(15) | 0.5557(4) | 0.048(4) |
| C122 | 0.5802(2) | 0.8766(17) | 0.5353(4) | 0.060(5) |
| H122 | 0.5122   | 0.9394   | 0.5373   | 0.072   |
| C132 | 0.6912(2) | 0.8737(17) | 0.5116(4) | 0.060(5) |
| H132 | 0.6977   | 0.9333   | 0.4969   | 0.072   |
| C142 | 0.7872(2) | 0.7856(16) | 0.5100(4) | 0.064(5) |
| H142 | 0.8624   | 0.7846   | 0.4939   | 0.077   |
| C152 | 0.7822(2) | 0.6934(15) | 0.5313(4) | 0.062(5) |
| H152 | 0.8524   | 0.6321   | 0.5296   | 0.074   |
| C162 | 0.6722(2) | 0.6966(15) | 0.5541(4) | 0.052(4) |
| C212 | 0.3732(2) | 0.6599(15) | 0.5780(4) | 0.054(4) |
| C222 | 0.2162(2) | 0.6401(16) | 0.5770(4) | 0.064(5) |
| H222 | 0.1442   | 0.7007   | 0.5788   | 0.077   |
| C232 | 0.1622(2) | 0.5280(17) | 0.5733(5) | 0.073(6) |
| H232 | 0.0546   | 0.5123   | 0.5724   | 0.088   |
| C242 | 0.2702(2) | 0.4418(18) | 0.5712(5) | 0.077(6) |
| H242 | 0.2350   | 0.3663   | 0.5687   | 0.092   |
| C252 | 0.4252   | 0.4636(17) | 0.5725(4) | 0.068(5) |
Table S9. Crystal data and structure refinement for T-BTBT (γ).

| Property                        | Value                  |
|---------------------------------|------------------------|
| Empirical formula               | C_{28}H_{16}S_{2}      |
| Formula weight                  | 416.53                 |
| Temperature                     | 200(2) K               |
| Wavelength                      | 0.71073 Å              |
| Crystal system                  | orthorhombic           |
| Space group                     | Pca2_1                 |
| Z                               | 8                      |
| Unit cell dimensions            |                         |
| a                               | 39.842(5) Å            |
| α                               | 90 deg.                |
| b                               | 8.3401(11) Å           |
| β                               | 90 deg.                |

Figure S53. Thermal atomic displacement ellipsoid plot of the asymmetric unit of T-BTBT (γ). The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.
Volume: 4001.0(8) Å^3  
Density (calculated): 1.38 g/cm^3  
Absorption coefficient: 0.28 mm^{-1}  
Crystal shape: thin plate  
Crystal size: 0.300 x 0.171 x 0.084 mm^3  
Crystal colour: colourless  
Theta range for data collection: 1.0 to 22.0 deg.  
Index ranges: -40 ≤ h ≤ 41, -6 ≤ k ≤ 8, -11 ≤ l ≤ 12  
Reflections collected: 10239  
Independent reflections: 4190 (R(int) = 0.0946)  
Observed reflections: 2455 (I > 2σ(I))  
Absorption correction: Semi-empirical from equivalents  
Max. and min. transmission: 0.96 and 0.81  
Refinement method: Full-matrix least-squares on F^2  
Data/restraints/parameters: 4190 / 2469 / 590  
Goodness-of-fit on F^2: 1.07  
Final R indices (I>2σ(I)): R1 = 0.083, wR2 = 0.184  
Absolute structure parameter: 0.58(19)  
Largest diff. peak and hole: 0.36 and -0.41 eÅ^-3

Table S10. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for T-BTBT (γ). Ueq is defined as one third of the trace of the orthogonalized Uij tensor.

| Atom | x     | y     | z     | Ueq  |
|------|-------|-------|-------|------|
| S11  | 0.5575(1) | 0.3278(7) | 0.4973(5) | 0.0397(15) |
| S21  | 0.5442(1) | 0.0225(6) | 0.2242(5) | 0.0399(15) |
| C11  | 0.6843(3) | 0.494(2)  | 0.3886(12) | 0.045(4)   |
| H11  | 0.6852   | 0.5654   | 0.4552   | 0.054      |
| C21  | 0.6825(3) | 0.309(2)  | 0.2162(13) | 0.041(4)   |
| H21  | 0.6817   | 0.2368   | 0.1497   | 0.049      |
| C111 | 0.7131(3) | 0.3743(16) | 0.3832(11) | 0.054(5)   |
| C121 | 0.7390(4) | 0.358(2)  | 0.4599(11) | 0.096(9)   |
| H121 | 0.7395   | 0.4242   | 0.5241   | 0.115      |
| C131 | 0.7640(4) | 0.245(3)  | 0.4428(13) | 0.127(12)  |
| H131 | 0.7817   | 0.2333   | 0.4952   | 0.152      |
| C141 | 0.7632(4) | 0.148(2)  | 0.3489(15) | 0.121(10)  |
| H141 | 0.7803   | 0.0701   | 0.3372   | 0.145      |
| C151 | 0.7373(4) | 0.1640(19) | 0.2722(12) | 0.074(7)   |
| H151 | 0.7368   | 0.0977   | 0.2080   | 0.089      |
| C161 | 0.7123(3) | 0.2774(18) | 0.2894(10) | 0.049(5)   |
| C211 | 0.6851(3) | 0.5853(16) | 0.2784(8)  | 0.047(5)   |
| C221 | 0.6851(3) | 0.7508(15) | 0.2649(10) | 0.057(6)   |
| H221 | 0.6855   | 0.8189   | 0.3281   | 0.068      |
| C231 | 0.6845(3) | 0.8166(12) | 0.1588(12) | 0.052(6)   |
| H231 | 0.6846   | 0.9297   | 0.1495   | 0.062      |
| C241 | 0.6839(4) | 0.7169(16) | 0.0663(9)  | 0.052(6)   |
| H241 | 0.6835   | 0.7618   | -0.0061  | 0.063      |
| C251 | 0.6839(3) | 0.5514(15) | 0.0799(8)  | 0.043(5)   |
| H251 | 0.6835   | 0.4832   | 0.0167   | 0.051      |
| C261 | 0.6845(3) | 0.4856(12) | 0.1859(10) | 0.044(5)   |
| C311 | 0.6519(2) | 0.3982(13) | 0.3793(9)  | 0.030(4)   |
| C321 | 0.6238(3) | 0.4107(13) | 0.4472(8)  | 0.028(4)   |
| H321 | 0.6242   | 0.4805   | 0.5096   | 0.034      |
| C331 | 0.5953(2) | 0.3213(13) | 0.4238(9)  | 0.025(4)   |
| C341 | 0.5948(2) | 0.2193(12) | 0.3325(9)  | 0.022(4)   |
| C351 | 0.6229(2) | 0.2068(12) | 0.2646(8)  | 0.022(4)   |
| H351 | 0.6226   | 0.1370   | 0.2022   | 0.026      |
| C361 | 0.6515(2) | 0.2962(14) | 0.2880(9)  | 0.031(4)   |
C37 0.5622(3)  0.152(2)  0.3219(13)  0.031(4)
C38 0.5394(4)  0.196(2)  0.4018(13)  0.033(4)
C41 0.5065(2)  0.1289(16)  0.3878(10)  0.040(5)
C42 0.5061(2)  0.0300(16)  0.2950(10)  0.039(4)
C43 0.4772(3)  -0.0556(14)  0.2684(10)  0.041(5)
H43 0.4769    -0.1232  0.2049  0.049
C44 0.4488(2)  -0.0421(16)  0.3347(12)  0.046(5)
H44 0.4291    -0.1006  0.3165  0.055
C45 0.4492(3)  0.0568(18)  0.4275(11)  0.057(6)
H45 0.4298    0.0660  0.4728  0.068
C46 0.4781(3)  0.1424(17)  0.4541(9)  0.050(6)
H46 0.4783    0.2100  0.5176  0.060
S1  0.4788(4)  0.237(2)  0.5039(17)  0.023(5)
S2  0.4671(5)  -0.062(2)  0.2310(17)  0.017(6)
C1  0.5999(7)  0.463(4)  0.387(3)  0.038(15)
H1  0.5994    0.5332  0.4537  0.046
C2  0.6009(7)  0.281(4)  0.213(3)  0.021(13)
H2  0.6015    0.2104  0.1463  0.025
C11 0.6317(8)  0.363(5)  0.377(3)  0.026(11)
C12 0.6584(9)  0.360(5)  0.451(3)  0.027(14)
H12 0.6581    0.4265  0.5154  0.032
C13 0.6857(8)  0.261(6)  0.431(4)  0.036(15)
H13 0.7040    0.2586  0.4818  0.044
C14 0.6863(8)  0.164(5)  0.337(4)  0.025(13)
H14 0.7049    0.0957  0.3236  0.030
C15 0.6595(9)  0.167(5)  0.263(3)  0.025(13)
H15 0.6599    0.1008  0.1989  0.030
C16 0.6322(7)  0.267(5)  0.283(3)  0.006(12)
C21 0.5994(11) 0.555(3)  0.277(2)  0.030(18)
C22 0.5992(12) 0.721(3)  0.265(3)  0.033(19)
H22 0.6004    0.7875  0.3294  0.039
C23 0.5973(13) 0.790(3)  0.160(4)  0.028(19)
H23 0.5972    0.9031  0.1526  0.034
C24 0.5956(14) 0.693(5)  0.067(3)  0.042(2)
H24 0.5943    0.7394  -0.0049  0.045
C25 0.5958(13) 0.527(4)  0.078(2)  0.042(2)
H25 0.5946    0.4602  0.0143  0.045
C26 0.5977(11) 0.458(3)  0.183(3)  0.011(15)
C31 0.5695(8)  0.354(5)  0.376(3)  0.047(12)
C32 0.5420(8)  0.351(6)  0.447(3)  0.060(18)
H32 0.5410    0.4236  0.5079  0.071
C33 0.5161(8)  0.243(6)  0.429(3)  0.037(13)
C34 0.5176(8)  0.137(6)  0.340(4)  0.036(12)
C35 0.5450(8)  0.140(5)  0.269(3)  0.039(13)
H35 0.5460    0.0674  0.2080  0.047
C36 0.5709(7)  0.248(5)  0.287(3)  0.027(13)
C37 0.4849(9)  0.070(9)  0.326(5)  0.043(12)
C38 0.4613(10) 0.109(10)  0.407(5)  0.041(14)
C41 0.4288(7)  0.033(6)  0.396(3)  0.039(16)
C42 0.4284(7)  -0.055(6)  0.298(3)  0.043(14)
C43 0.3991(8)  -0.132(6)  0.265(3)  0.030(18)
H43 0.3988    -0.1916  0.1975  0.035
C44 0.3703(7)  -0.121(7)  0.329(4)  0.08(3)
H44 0.3503    -0.1732  0.3063  0.092
C45 0.3708(7)  -0.033(7)  0.427(4)  0.01(2)
H45 0.3511    -0.0255  0.4715  0.017
C46 0.4000(8)  0.044(6)  0.461(3)  0.028(19)
H46 0.4003    0.1038  0.5280  0.034
S12 0.5182(1)  0.7810(6)  0.5048(5)  0.0369(15)
S22 0.5065(1)  0.4785(7)  0.7807(5)  0.0398(16)
C12 0.6414(4)  0.982(2)  0.6170(13)  0.051(5)
|   |       |       |       |       |
|---|-------|-------|-------|-------|
| H12 | 0.6413 | 1.0536 | 0.5504 | 0.061  |
| C22 | 0.6419(4) | 0.796(2) | 0.7905(13) | 0.045(4)  |
| H22 | 0.6420 | 0.7235 | 0.8569 | 0.054  |
| C112 | 0.6721(3) | 0.8780(18) | 0.6263(12) | 0.057(5)  |
| C122 | 0.6994(4) | 0.882(2) | 0.5546(11) | 0.082(7)  |
| H122 | 0.6994 | 0.9539 | 0.4933 | 0.098  |
| C132 | 0.7266(3) | 0.781(2) | 0.5724(13) | 0.098(8)  |
| H132 | 0.7453 | 0.7839 | 0.5234 | 0.118  |
| C142 | 0.7265(3) | 0.676(2) | 0.6621(15) | 0.087(7)  |
| H142 | 0.7451 | 0.6070 | 0.6743 | 0.105  |
| C152 | 0.6992(4) | 0.6720(19) | 0.7338(13) | 0.078(7)  |
| H152 | 0.6991 | 0.6002 | 0.7951 | 0.094  |
| C162 | 0.6720(3) | 0.7730(19) | 0.7159(11) | 0.058(5)  |
| C212 | 0.6411(3) | 1.0713(16) | 0.7276(8) | 0.045(5)  |
| C222 | 0.6401(3) | 1.2368(15) | 0.7408(9) | 0.056(6)  |
| H222 | 0.6402 | 1.3047 | 0.6775 | 0.067  |
| C232 | 0.6390(4) | 1.3029(12) | 0.8467(12) | 0.051(6)  |
| H232 | 0.6383 | 1.4160 | 0.8557 | 0.061  |
| C242 | 0.6389(4) | 1.2036(16) | 0.9394(9) | 0.049(6)  |
| H242 | 0.6381 | 1.2488 | 1.0118 | 0.059  |
| C252 | 0.6399(4) | 1.0381(15) | 0.9262(8) | 0.044(6)  |
| H252 | 0.6398 | 0.9702 | 0.9895 | 0.053  |
| C262 | 0.6410(3) | 0.9791(12) | 0.8203(10) | 0.041(5)  |
| C312 | 0.6114(2) | 0.8707(14) | 0.6241(9) | 0.040(4)  |
| C322 | 0.5834(3) | 0.8751(14) | 0.5550(8) | 0.037(5)  |
| H322 | 0.5834 | 0.9429 | 0.4915 | 0.044  |
| C332 | 0.5556(2) | 0.7804(15) | 0.5786(9) | 0.026(4)  |
| C342 | 0.5558(2) | 0.6812(13) | 0.6713(10) | 0.025(4)  |
| C352 | 0.5837(3) | 0.6768(13) | 0.7405(8) | 0.032(4)  |
| H352 | 0.5837 | 0.6090 | 0.8039 | 0.038  |
| C362 | 0.6115(2) | 0.7715(15) | 0.7169(9) | 0.038(4)  |
| C372 | 0.5242(3) | 0.6052(19) | 0.6819(12) | 0.021(4)  |
| C382 | 0.5018(4) | 0.643(2) | 0.5986(13) | 0.025(4)  |
| C412 | 0.4690(2) | 0.5730(15) | 0.6136(10) | 0.032(4)  |
| C422 | 0.4688(2) | 0.4796(16) | 0.7092(10) | 0.035(4)  |
| C432 | 0.4400(3) | 0.3958(15) | 0.7388(9) | 0.046(5)  |
| H432 | 0.4398 | 0.3319 | 0.8041 | 0.055  |
| C442 | 0.4114(2) | 0.4054(16) | 0.6726(12) | 0.052(6)  |
| H442 | 0.3918 | 0.3481 | 0.6930 | 0.063  |
| C452 | 0.4117(3) | 0.4988(18) | 0.5772(11) | 0.060(7)  |
| H452 | 0.3922 | 0.5054 | 0.5321 | 0.072  |
| C462 | 0.4405(3) | 0.5826(16) | 0.5476(9) | 0.046(5)  |
| H462 | 0.4407 | 0.6465 | 0.4823 | 0.055  |
| S1B2 | 0.5957(4) | 0.876(2) | 0.5163(16) | 0.013(5)  |
| S2B2 | 0.5816(4) | 0.561(2) | 0.7801(16) | 0.026(5)  |
| C1B2 | 0.7248(7) | 1.009(4) | 0.619(3) | 0.064(17)  |
| H1B2 | 0.7259 | 1.0852 | 0.5552 | 0.077  |
| C2B2 | 0.7221(7) | 0.812(4) | 0.786(3) | 0.048(16)  |
| H2B2 | 0.7209 | 0.7356 | 0.8497 | 0.058  |
| C1B2 | 0.7533(9) | 0.889(5) | 0.622(3) | 0.058(19)  |
| C1B2 | 0.7790(10) | 0.875(5) | 0.544(3) | 0.025(18)  |
| H1B2 | 0.7801 | 0.9462 | 0.4830 | 0.030  |
| C1B2 | 0.8032(10) | 0.756(6) | 0.557(4) | 0.02(2)  |
| H1B2 | 0.8208 | 0.7461 | 0.5037 | 0.027  |
| C14B2 | 0.8017(10) | 0.651(5) | 0.646(4) | 0.04(2)  |
| H14B2 | 0.8182 | 0.5700 | 0.6547 | 0.046  |
| C15B2 | 0.7760(10) | 0.665(5) | 0.724(4) | 0.032(19)  |
| H15B2 | 0.7750 | 0.5940 | 0.7851 | 0.038  |
| C16B2 | 0.7518(8) | 0.784(5) | 0.711(3) | 0.058(17)  |
| C21B2 | 0.7257(11) | 1.092(4) | 0.733(2) | 0.027(18)  |
| C22B2 | 0.7279(12) | 1.256(4) | 0.752(3) | 0.04(2)  |
Figure S54. Thermal atomic displacement ellipsoid plot of the asymmetric unit of T-BTBT (δ₁). The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

Table S11. Crystal data and structure refinement for T-BTBT (δ₁).

| Property                                  | Value                  |
|-------------------------------------------|------------------------|
| Empirical formula                         | C_{28}H_{16}S_{2}      |
| Formula weight                            | 416.53                 |
| Temperature                               | 200(2) K               |
| Wavelength                                | 0.71073 Å              |
| Crystal system                            | orthorhombic           |
| Space group                               | Pca2₁                  |
| Z                                         | 4                      |
| Unit cell dimensions                      |                        |
| a = 8.5147(14) Å                         | 90 deg.                |
| b = 14.754(3) Å                          | 90 deg.                |
| c = 15.788(3) Å                          | 90 deg.                |
| Volume                                    | 1983.3(6) Å³           |
| Density (calculated)                      | 1.39 g/cm³             |
| Absorption coefficient                    | 0.28 mm⁻¹              |
| Crystal shape                             | little                 |
| Crystal size                              | 0.201 x 0.117 x 0.079 mm³|
| Crystal colour                            | colourless             |
Theta range for data collection 1.4 to 28.4 deg.
Index ranges -11≤h≤11, -19≤k≤19, -18≤l≤21
Reflections collected 14768
Independent reflections 4530 (R(int) = 0.0687)
Observed reflections 3394 (I > 2σ(I))
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.96 and 0.80
Refinement method Full-matrix least-squares on F^2
Data/restraints/parameters 4530 / 1 / 280
Goodness-of-fit on F^2 1.07
Final R indices (I>2σ(I)) R1 = 0.047, wR2 = 0.102
Absolute structure parameter 0.05(6)
Largest diff. peak and hole 0.28 and -0.35 eÅ^3

Table S12. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for T-BTBT (δ1).
U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| Atom | x   | y   | z   | U_{eq} |
|------|-----|-----|-----|--------|
| S1   | 0.6965(1) | 0.5549(1) | 0.5040(1) | 0.0279(3) |
| S2   | 0.9527(1) | 0.4284(1) | 0.6976(1) | 0.0309(4) |
| C1   | 0.4580(5) | 0.2454(3) | 0.3762(3) | 0.0274(10) |
| H1   | 0.3960 | 0.2824 | 0.3350 | 0.033 |
| C2   | 0.6203(5) | 0.1491(3) | 0.4826(3) | 0.0263(10) |
| H2   | 0.6825 | 0.1119 | 0.5236 | 0.032 |
| C11  | 0.5635(5) | 0.1750(3) | 0.3338(3) | 0.0274(10) |
| C12  | 0.5789(6) | 0.1602(3) | 0.2477(3) | 0.0337(12) |
| H12  | 0.5198 | 0.1950 | 0.2084 | 0.040 |
| C13  | 0.6813(6) | 0.0940(3) | 0.2195(4) | 0.0428(13) |
| H13  | 0.6921 | 0.0838 | 0.1604 | 0.051 |
| C14  | 0.7670(7) | 0.0431(4) | 0.2747(3) | 0.0431(14) |
| H14  | 0.8364 | -0.0021 | 0.2539 | 0.052 |
| C15  | 0.7530(6) | 0.0572(3) | 0.3622(3) | 0.0373(12) |
| H15  | 0.8128 | 0.0220 | 0.4009 | 0.045 |
| C16  | 0.6510(5) | 0.1232(3) | 0.3916(3) | 0.0266(10) |
| C21  | 0.3561(5) | 0.1926(3) | 0.4382(3) | 0.0268(10) |
| C22  | 0.1939(5) | 0.1940(3) | 0.4427(3) | 0.0334(12) |
| H22  | 0.1346 | 0.2289 | 0.4035 | 0.040 |
| C23  | 0.1185(5) | 0.1438(3) | 0.5049(4) | 0.0378(12) |
| H23  | 0.0071 | 0.1442 | 0.5081 | 0.045 |
| C24  | 0.2043(6) | 0.0932(3) | 0.5625(4) | 0.0381(12) |
| H24  | 0.1513 | 0.0596 | 0.6052 | 0.046 |
| C25  | 0.3669(5) | 0.0911(3) | 0.5582(3) | 0.0295(10) |
| H25  | 0.4254 | 0.0563 | 0.5978 | 0.035 |
| C26  | 0.4434(5) | 0.1399(3) | 0.4959(3) | 0.0246(9) |
| C31  | 0.5677(5) | 0.3021(3) | 0.4318(3) | 0.0251(10) |
| C32  | 0.5789(5) | 0.3960(3) | 0.4307(3) | 0.0272(10) |
| H32  | 0.5228 | 0.4307 | 0.3901 | 0.033 |
| C33  | 0.6740(5) | 0.4378(3) | 0.4904(3) | 0.0257(11) |
| C34  | 0.7578(5) | 0.3863(3) | 0.5517(3) | 0.0263(10) |
| C35  | 0.7478(5) | 0.2915(3) | 0.5503(3) | 0.0269(10) |
| H35  | 0.8049 | 0.2563 | 0.5901 | 0.032 |
| C36  | 0.6540(5) | 0.2496(3) | 0.4903(3) | 0.0246(9) |
| C37  | 0.8360(5) | 0.4468(3) | 0.6091(3) | 0.0278(10) |
| C38  | 0.8124(5) | 0.5369(3) | 0.5936(3) | 0.0286(10) |
| C41  | 0.8863(6) | 0.5960(3) | 0.6528(3) | 0.0319(11) |
| C42  | 0.9703(5) | 0.5456(3) | 0.7135(3) | 0.0325(12) |
| C43  | 1.0569(6) | 0.5890(4) | 0.7761(4) | 0.0424(14) |
| H43  | 1.1162 | 0.5550 | 0.8160 | 0.051 |
| C44  | 1.0551(6) | 0.6831(4) | 0.7793(4) | 0.0476(15) |
Table S13. Crystal data and structure refinement for T-BTBT ($\delta_2$).

| Parameter                                | Value                        |
|------------------------------------------|------------------------------|
| Empirical formula                        | C$_{28}$H$_{16}$S$_2$        |
| Formula weight                           | 416.53                       |
| Temperature                              | 200(2) K                     |
| Wavelength                               | 0.71073 Å                    |
| Crystal system                           | monoclinic                   |
| Space group                              | C2/c                         |
| Z                                        | 8                            |
| Unit cell dimensions                     | a = 29.1818(16) Å, $\alpha$ = 90 deg. |
|                                           | b = 8.3041(5) Å, $\beta$ = 98.0981(14) deg. |
|                                           | c = 16.3277(9) Å, $\gamma$ = 90 deg. |
| Volume                                   | 3917.2(4) Å$^3$              |
| Density (calculated)                     | 1.41 g/cm$^3$                |
| Absorption coefficient                   | 0.28 mm$^{-1}$               |
| Crystal shape                            | brick                        |
| Crystal size                             | 0.163 x 0.102 x 0.088 mm$^3$ |
| Crystal colour                           | colourless                   |
| Theta range for data collection          | 1.4 to 26.8 deg.             |
| Index ranges                             | -36 ≤ h ≤ 36, -10 ≤ k ≤ 10, -20 ≤ l ≤ 20 |
| Reflections collected                    | 27016                        |
| Independent reflections                  | 4164 (R(int) = 0.0842)       |
| Observed reflections                     | 2847 (I > 2$\sigma$(I))     |
| Absorption correction                    | Semi-empirical from equivalents |
| Max. and min. transmission               | 0.96 and 0.86                |
| Refinement method                        | Full-matrix least-squares on F$^2$ |
| Data/restraints/parameters               | 4164 / 0 / 280               |
| Goodness-of-fit on F$^2$                 | 1.03                         |
| Final R indices (I$>$2$\sigma$(I))       | R1 = 0.047, wR2 = 0.110      |
| Largest diff. peak and hole              | 0.41 and -0.27 eÅ$^3$        |

Figure S55. Thermal atomic displacement ellipsoid plot of the asymmetric unit of T-BTBT ($\delta_2$). The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.
Table S14. Atomic coordinates and equivalent isotropic displacement parameters (Å²) for T-BTBT (δ2).

$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atom | x       | y       | z       | $U_{eq}$ |
|------|---------|---------|---------|----------|
| S1   | 0.2207(1)| 0.7288(1)| 0.3031(1) | 0.0318(2) |
| S2   | 0.2731(1) | 1.0503(1) | 0.4916(1) | 0.0299(2) |
| C1   | 0.3795(1) | 0.6842(3) | 0.1755(1) | 0.0324(6) |
| H1   | 0.3642   | 0.6018   | 0.1361   | 0.039     |
| C2   | 0.4194(1) | 0.8974(3) | 0.2769(1) | 0.0298(5) |
| H2   | 0.4348   | 0.9801   | 0.3160   | 0.036     |
| C11  | 0.4040(1) | 0.8145(3) | 0.1332(1) | 0.0308(6) |
| C12  | 0.4079(1) | 0.8227(3) | 0.0494(2) | 0.0400(6) |
| H12  | 0.3934   | 0.7445   | 0.0119   | 0.048     |
| C13  | 0.4334(1) | 0.9479(3) | 0.0214(2) | 0.0443(7) |
| H13  | 0.4367   | 0.9537   | -0.0355  | 0.053     |
| C14  | 0.4539(1) | 1.0634(3) | 0.0751(2) | 0.0420(7) |
| H14  | 0.4708   | 1.1490   | 0.0548   | 0.050     |
| C15  | 0.4500(1) | 1.0545(3) | 0.1589(2) | 0.0340(6) |
| H15  | 0.4643   | 1.1335   | 0.1961   | 0.041     |
| C16  | 0.4254(1) | 0.9305(3) | 0.1876(1) | 0.0277(5) |
| C21  | 0.4158(1) | 0.6123(3) | 0.2420(1) | 0.0308(5) |
| C22  | 0.4258(1) | 0.4501(3) | 0.2545(2) | 0.0383(6) |
| H22  | 0.4105   | 0.3712   | 0.2185   | 0.046     |
| C23  | 0.4586(1) | 0.4047(3) | 0.3207(2) | 0.0453(7) |
| H23  | 0.4651   | 0.2937   | 0.3306   | 0.054     |
| C24  | 0.4819(1) | 0.5189(3) | 0.3722(2) | 0.0436(7) |
| H24  | 0.5050   | 0.4864   | 0.4161   | 0.052     |
| C25  | 0.4717(1) | 0.6823(3) | 0.3598(2) | 0.0360(6) |
| H25  | 0.4876   | 0.7613   | 0.3952   | 0.043     |
| C26  | 0.4382(1) | 0.7276(3) | 0.2958(1) | 0.0292(5) |
| C31  | 0.3460(1) | 0.7661(3) | 0.2256(2) | 0.0318(6) |
| C32  | 0.3002(1) | 0.7211(3) | 0.2249(2) | 0.0343(6) |
| H32  | 0.2856   | 0.6483   | 0.1846   | 0.041     |
| C33  | 0.2766(1) | 0.7858(3) | 0.2850(2) | 0.0333(6) |
| C34  | 0.2975(1) | 0.8957(3) | 0.3433(1) | 0.0284(5) |
| C35  | 0.3435(1) | 0.9483(3) | 0.3402(1) | 0.0315(6) |
| H35  | 0.3574   | 1.0280   | 0.3774   | 0.038     |
| C36  | 0.3676(1) | 0.8804(3) | 0.2818(1) | 0.0295(5) |
| C37  | 0.2673(1) | 0.9306(3) | 0.4038(2) | 0.0312(6) |
| C38  | 0.2265(1) | 0.8501(3) | 0.3908(2) | 0.0330(6) |
| C41  | 0.1966(1) | 0.8812(3) | 0.4522(2) | 0.0336(6) |
| C42  | 0.2177(1) | 0.9903(3) | 0.5105(2) | 0.0362(6) |
| C43  | 0.1960(1) | 1.0397(3) | 0.5758(2) | 0.0437(7) |
| H43  | 0.2107   | 1.1130   | 0.6159   | 0.052     |
| C44  | 0.1522(1) | 0.9803(3) | 0.5818(2) | 0.0456(7) |
| H44  | 0.1366   | 1.0153   | 0.6259   | 0.055     |
| C45  | 0.1307(1) | 0.8706(3) | 0.5248(2) | 0.0467(7) |
| H45  | 0.1007   | 0.8313   | 0.5305   | 0.056     |
| C46  | 0.1523(1) | 0.8182(3) | 0.4599(2) | 0.0410(7) |
| H46  | 0.1378   | 0.7419   | 0.4212   | 0.049     |
| S1B  | 0.2942(4) | 1.0713(11)| 0.4512(6) | 0.052(3)  |
| S2B  | 0.2010(4) | 0.7232(14)| 0.3450(8) | 0.068(4)  |
Figure S56. Thermal atomic displacement ellipsoid plot of the asymmetric unit of T-NTBT (α). The ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

Table S15. Crystal data and structure refinement for T-NTBT (α).

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Empirical formula               | C32H18S2                                   |
| Formula weight                  | 466.58                                     |
| Temperature                     | 200(2) K                                   |
| Wavelength                      | 0.71073 Å                                  |
| Crystal system                  | triclinic                                  |
| Space group                     | P 1                                       |
| Z                               | 2                                          |
| Unit cell dimensions            | a=7.2769(3) Å, b=8.0563(4) Å, c=19.7543(9) Å |
| Volume                          | 1088.06(9) Å                              |
| Density (calculated)            | 1.42 g/cm³                                 |
| Absorption coefficient          | 0.26 mm⁻¹                                  |
| Crystal shape                   | brick                                      |
| Crystal size                    | 0.193 x 0.150 x 0.115 mm³                  |
| Crystal colour                  | colourless                                 |
| Theta range for data collection | 1.1 to 26.4 deg.                           |
| Index ranges                    | -9≤h≤9, -10≤k≤10, -24≤l≤24                 |
| Reflections collected           | 15162                                      |
| Independent reflections         | 4460 (R(int) = 0.0237)                     |
| Observed reflections            | 3697 (I > 2σ(I))                           |
| Absorption correction           | Semi-empirical from equivalents            |
| Max. and min. transmission      | 0.97 and 0.93                             |
| Refinement method               | Full-matrix least-squares on F²           |
| Data/restraints/parameters      | 4460 / 968 / 396                           |
| Goodness-of-fit on F²           | 1.11                                       |
| Final R indices (I>2σ(I))       | R1 = 0.035, wR2 = 0.097                   |
| Largest diff. peak and hole     | 0.32 and -0.33 eÅ⁻³                        |

Table S16. Atomic coordinates and equivalent isotropic displacement parameters (Å²) for T-NTBT (α). Ueq is defined as one third of the trace of the orthogonalized Uij tensor.

| Atom  | x     | y     | z     | Ueq  |
|-------|-------|-------|-------|------|
| C11   | 0.0384(2) | 1.0748(2) | 0.1700(1) | 0.0252(4) |
| C12   | -0.0836(3) | 1.2347(2) | 0.1846(1) | 0.0325(4) |
| H12   | -0.2177   | 1.2464   | 0.1997   | 0.039  |
| C13   | -0.0067(3) | 1.3779(2) | 0.1767(1) | 0.0389(5) |
| H13   | -0.0894   | 1.4881   | 0.1862   | 0.047  |
| C14   | 0.1874(3) | 1.3620(3) | 0.1552(1) | 0.0408(5) |
| H14   | 0.2374    | 1.4612   | 0.1498   | 0.049  |
| C15   | 0.3111(3) | 1.2013(3) | 0.1412(1) | 0.0348(4) |
| H15   | 0.4453    | 1.1901   | 0.1266   | 0.042  |
| C16   | 0.2359(3) | 1.0581(2) | 0.1489(1) | 0.0277(4) |
| C21 | 0.0584(2) | 0.8333(2) | 0.1057(1) | 0.0247(4) |
|-----|-----------|-----------|-----------|-----------|
| C22 | -0.0471(3)| 0.7876(2) | 0.0634(1) | 0.0308(4) |
| H22 | -0.1825   | 0.8026    | 0.0762    | 0.037     |
| C23 | 0.0459(3) | 0.7194(2) | 0.0018(1) | 0.0357(4) |
| H23 | -0.0261   | 0.6880    | -0.0275   | 0.043     |
| C24 | 0.2426(3) | 0.6975(3) | -0.0165(1)| 0.0379(5) |
| H24 | 0.3057    | 0.6495    | -0.0582   | 0.045     |
| C25 | 0.3498(3) | 0.7451(2) | 0.0255(1) | 0.0348(4) |
| H25 | 0.4852    | 0.7301    | 0.0127    | 0.042     |
| C26 | 0.2564(3) | 0.8145(2) | 0.0862(1) | 0.0277(4) |
| S1  | 0.1010(1) | 0.4786(1) | 0.4116(1) | 0.0227(2) |
| S2  | 0.7043(1) | 0.3959(1) | 0.3762(1) | 0.0236(2) |
| C1  | -0.0213(5)| 0.9056(5) | 0.1753(2) | 0.0237(7) |
| H1  | -0.1637   | 0.9199    | 0.1884    | 0.028     |
| C2  | 0.3474(4) | 0.8691(4) | 0.1400(2) | 0.0242(5) |
| H2  | 0.4896    | 0.8554    | 0.1263    | 0.029     |
| C31 | 0.0980(4) | 0.7813(2) | 0.2279(1) | 0.0198(4) |
| C32 | 0.0263(3) | 0.6951(2) | 0.2887(1) | 0.0212(4) |
| H32 | -0.1084   | 0.7057    | 0.3013    | 0.025     |
| C33 | 0.1593(3) | 0.5913(2) | 0.3311(1) | 0.0198(4) |
| C34 | 0.3616(4) | 0.5736(3) | 0.3126(1) | 0.0195(5) |
| C35 | 0.4298(3) | 0.6610(2) | 0.2501(1) | 0.0220(4) |
| H35 | 0.5643    | 0.6499    | 0.2364    | 0.026     |
| C36 | 0.2985(4) | 0.7630(3) | 0.2088(1) | 0.0213(4) |
| C37 | 0.4607(3) | 0.4659(2) | 0.3663(1) | 0.0214(4) |
| C38 | 0.3430(3) | 0.4068(2) | 0.4214(1) | 0.0211(4) |
| C41 | 0.4413(3) | 0.2992(2) | 0.4755(1) | 0.0200(4) |
| C42 | 0.6454(3) | 0.2858(2) | 0.4583(1) | 0.0210(4) |
| C43 | 0.7725(3) | 0.1947(2) | 0.5028(1) | 0.0236(4) |
| H43 | 0.9062    | 0.1902    | 0.4912    | 0.028     |
| C44 | 0.7024(4) | 0.1079(3) | 0.5658(1) | 0.0224(5) |
| C45 | 0.8274(4) | 0.0108(4) | 0.6140(1) | 0.0281(6) |
| H45 | 0.9607    | 0.0089    | 0.6052    | 0.034     |
| C46 | 0.7568(5) | -0.0801(5)| 0.6732(2) | 0.0312(8) |
| H46 | 0.8416    | -0.1434   | 0.7050    | 0.037     |
| C47 | 0.5599(6) | -0.0803(7)| 0.6872(2) | 0.0296(8) |
| H47 | 0.5143    | -0.1483   | 0.7271    | 0.036     |
| C48 | 0.4341(6) | 0.0167(7) | 0.6437(3) | 0.0292(9) |
| H48 | 0.3006    | 0.0202    | 0.6548    | 0.035     |
| C49 | 0.5016(4) | 0.1125(3) | 0.5818(1) | 0.0215(5) |
| C50 | 0.3735(3) | 0.2111(2) | 0.5362(1) | 0.0224(4) |
| H50 | 0.2394    | 0.2169    | 0.5474    | 0.027     |
| S1B | 0.6711(6) | 0.4758(5) | 0.3333(2) | 0.0339(12)|
| S2B | 0.1409(7)| 0.4175(6) | 0.4429(3) | 0.0374(12)|
| C1B | 0.3664(4) | 0.9063(3) | 0.1243(11)| 0.032(7)  |
| H1B | 0.4967    | 0.9167    | 0.1008    | 0.039     |
| C2B | 0.0164(4) | 0.8874(4) | 0.1817(16)| 0.022(7)  |
| H2B | -0.1152   | 0.8794    | 0.2057    | 0.027     |
| C31B| 0.361(2)  | 0.780(2)  | 0.1881(8) | 0.021(4)  |
| C32B| 0.524(2)  | 0.694(2)  | 0.2208(7) | 0.034(4)  |
| H32B| 0.6500    | 0.7048    | 0.2016    | 0.041     |
| C33B| 0.4882(19)| 0.5907(19)| 0.2835(7) | 0.030(3)  |
| C34B| 0.2984(19)| 0.583(2)  | 0.3165(7) | 0.006(4)  |
| C35B| 0.140(2)  | 0.675(2)  | 0.2831(7) | 0.033(4)  |
| H35B| 0.0117    | 0.6728    | 0.3032    | 0.039     |
| C36B| 0.178(2)  | 0.768(2)  | 0.2197(7) | 0.016(4)  |
| C37B| 0.3146(18)| 0.478(2)  | 0.3815(7) | 0.033(3)  |
| C38B| 0.4975(19)| 0.419(2)  | 0.3979(7) | 0.035(4)  |
| C41B| 0.512(2)  | 0.3097(19)| 0.4648(7) | 0.013(4)  |
| C42B| 0.3215(19)| 0.2970(17)| 0.4940(6) | 0.025(3)  |
| C43B| 0.285(2)  | 0.196(2)  | 0.5553(7) | 0.029(4)  |
6 Theoretical Calculations

6.1 Electronic Coupling Calculation (DFTB)

The calculation of the electronic couplings requires quantum chemical methods. In this work, the semi-empirical Tight-Binding Density Functional theory (DFTB) method was applied.\cite{23a} This method is derived from density functional theory (DFT) but roughly 2-3 orders of magnitude faster than standard GGA-DFT methods with medium sized basis sets. Therefore, the individual molecules, which contain 46-52 atoms, can be calculated in reasonable computational time, allowing to compute the extensive scans for the dimers containing up to 104 atoms.

For the calculation of the charge transfer couplings, the complex is separated into fragments, corresponding to the individual molecules. For each of the \( M \) fragments (molecules, indexed as \( m \)), we compute the molecular orbitals \( \psi_i^m \)

\[
\psi_i^m = \sum_{\mu} c_i^m \chi_\mu
\]

Here, the \( i \)-th molecular orbital (FO) of fragment \( m \) is expressed in an atomic-orbital-like basis set \( \chi_\mu \) with expansion coefficients \( c_i^m \). Usually, it is sufficient to consider for each fragment one orbital (FO), which will be the HOMO for a hole transfer and the LUMO for an electron transfer (\( \psi_i^LUMO \) or \( \psi_i^HOMO \)). In special cases, more orbitals (like HOMO-1 etc.) can also be taken into account. This can be especially relevant, if the energy difference between the orbitals is small. The Hamiltonian matrix is built from the FO coefficients, e.g. for the coupling of the HOMO orbitals one gets

\[
H_{mn} = \langle \psi_m^{HOMO} | \hat{H} | \psi_n^{HOMO} \rangle = \sum_{\mu} \sum_{\nu} c_{\mu}^{HOMO m} c_{\nu}^{HOMO n} \bar{H}_{\mu \nu}
\]

The off-diagonal elements of the Hamiltonian matrix correspond to the electronic couplings between the individual fragments, the diagonal elements are the orbital energies. \( \bar{H}_{\mu \nu} \) is the Hamiltonian in the atomic-orbital basis.

Using the fast, semi-empirical DFTB method to compute \( \bar{H}_{\mu \nu} \) leads to a highly efficient scheme to compute couplings, allowing to treat large systems and investigate a multitude of conformations. In a recent extended benchmark study it has been shown, that this approximate methodology reproduces the couplings, computed with high level \( \text{ab initio} \) methods for a large molecular test set, with high accuracy.\cite{23b,c}
Beside the successful benchmark of the coupling calculation, this FO-DFTB approach was also used to perform direct simulations of the charge carrier in different systems e.g. organic semiconductors, DNA and proteins, which reproduced the experimental results.\[23d-k\]

DFT is known to be an approximate method, which shows excellent performance for many molecular properties like geometries or thermochemistry data, but, on the other hand, is known to exhibit several short comings. The most prominent among these is the self-interaction error of DFT, present in DFT functionals using the generalized gradient approximation (GGA), which leads to a wrong estimate of orbital energies. Compared to ab initio methods, not only the absolute energies are deviant, but often also the relative ordering of the orbitals. This behavior of GGA functionals like BLYP or PBE is - only partially – corrected for when using hybrid functionals like B3LPY.

Typically, the energies of occupied orbitals are too high (by several eV!), and the energy differences between orbitals are too small and/or orbitals are interchanged. The character and shape of the orbitals, however, is preserved. There, in DFT-GGA often the HOMO orbital has a $\sigma$-symmetry, while the correct $\pi$-orbital can be found as HOMO-1 or HOMO-2. This deficiency is particularly common in large molecules like those considered in this work (in fact, the energy differences between the orbitals is as little as 0.02–0.15 eV). To compute the correct charge transfer couplings, the respective orbitals with the proper symmetry have to be used. This problem also occurs in DFTB, since it is derived from DFT-GGA using a PBE functional.\[32\]

To this end, each molecule was placed in the x,y-plane of the coordinate system, and the contribution of the $\pi_{z}$-orbitals on the heavy atoms of the conjugated system to the LUMO, HOMO, ..., HOMO-3 was calculated from their LCAO coefficients as $\sum_{\mu} (c_{\mu \pi_{z}})^{2}$. The orbital was considered to have $\pi$-symmetry if that value exceeded a threshold (0.1). The DFTB+ program was employed and to visualize the orbitals and to calculate the coefficients.

6.2 Calculation of Reorganization energies

Reorganization energies for hole transport were calculated by DFT-B3LYP/6-31G*. This method is more accurate than DFTB and is a standard method to calculate reorganization energies. It is a well-known method for geometry optimization and it has been shown that its result is in very good agreement with experimental data. Pure GGA functionals underestimate lambda, this also holds true for other functionals, such as DFTB and for DFT-PBE, BLYP etc. So, hybride functionals or range separated functionals have to be used. A standard functional in the literature is therefore B3LYP.\[33\]

7 Transistor Fabrication

Field-effect transistors were fabricated via manual lamination of PVD-grown crystals onto prefabricated electrode structures, forming a bottom gate / bottom contact architecture. The substrate is a heavily p-doped Si-wafer with 300 nm thermal silicon oxide as the gate dielectric, assuming a gate capacitance of 11.5 nF/cm². The substrate was sonicated in acetone and IPA for 10 minutes and blow dried afterwards. Electrodes were deposited through a shadow mask via electron-beam evaporation of 30 nm Pt electrodes with a 2 nm Ti adhesion layer underneath. Before crystal lamination the substrates were UV-Ozone treated for 10 minutes and rinsed with deionized water and blow dried with nitrogen. The finished device was transferred into...
a Nitrogen filled glovebox for electrical measurements using a Keysight B1500a semiconductor parameter analyzer (Integration was set to 3 powerline cycles and voltage step width was 1V). These devices were the best performing devices, indicating that the contacts still require optimization to enhance device performance and reliable charge carrier mobility extraction.

Figure S57. Optical bright field micrographs (a) and (d) show the thin crystals laminated onto the substrate with prefabricated electrodes underneath. Transfer characteristics of the devices in (b) and (e) show logarithmic transfer curves, measured at -5 V and -50 V drain bias. Hole mobilities were extracted from the slope of the respective curves in linear scale for the linear mobility and the square root of the drain current for the saturation mobility when sweeping from zero to negative gate bias. Output curves (c) and (f) show a relatively linear onset at low drain bias, indicating ohmic contact and saturation at higher drain biases.

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