The Influence of Molecular Geometry on the Efficiency of Thermally Activated Delayed Fluorescence.

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Supporting Information

S1. Electrochemistry.

The ionization potential (IP) and electron affinity (EA) were determined from the onset of the redox peaks, assuming the potentials are expressed on the absolute potential scale, i.e. with respect to the vacuum level. The absolute potential of Fc/Fc⁺ in non-aqueous electrolytes is 5.1 V.[S1-S3] This leads to the following equations:

IP(eV) = |e|(E_{ox(onset)} + 5.1)  \quad (1)
EA(eV) = -|e|(E_{red(onset)} + 5.1)  \quad (2)

The energies associated with the HOMO and LUMO orbitals were estimated from the EA and IP potentials,[S3, S4] using an electrochemical cell containing a platinum electrode with 1 mm diameter of working area as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum coil as an auxiliary electrode. Cyclic voltammetry measurements were conducted at room temperature at a scan rate of 50 mV/s, calibrated against a ferrocene/ferrocenium redox couple. Solvents were dried before use, and electrochemical measurements were conducted in 1.0 mM concentrations of all compounds. Electrochemical studies were undertaken in 0.1 M solutions of Bu₄NBF₄, 99% (Sigma Aldrich) in dichloromethane (DCM), THF or DMF solvent, CHROMASOLV®, 99.9% (Sigma Aldrich) at room temperature. Although, the presented CVs were recorded in dichloromethane based electrolyte, additional checks were performed in THF and DMF for the reductions. No significant change in the potential was observed and therefore the data presented can be deemed to be reliable.
All of the investigated compounds were electroactive and showed both oxidation and reduction processes (Figure S1.1). The larger change in the IP energy is observed with increasing the size of the alkyl group (compounds 1-4, from -5.4 → -6.1 eV) (Figures S1.1a, and S1.2). This is consistent with the alkyl group inducing changes in conformation of the phenothiazine. Interestingly, there is almost no difference in energy of the IP and EA potentials between t-butyl mono-substitution and methyl bi-substitution (Figure S1.2, compounds 4 and 5).

![Figure S1.1 - Cyclic voltammetry of 2 mM concentration of investigated compounds in 0.1M Bu$_4$NBF$_4$/DCM. Measurement conditions: scan rate 50 mV/s, Ag/AgCl – quasi-reference electrode, calibrated against a ferrocene/ferrocenium redox couple.](image)

When the alkyl group was connected to acceptor instead of the donor unit there almost no change in the IP energy is observed. However, there is a small change in the EA energy. In our present work the substituents are systematically increased in steric bulk at the same position on the donor. It is expected that the electron donating strength in the present series of compounds will not vary significantly as the difference in inductive effects of Me, iPr, tBu are subtle and minor. It is likely that both effects (bulk and electron-donating ability) are contributing simultaneously and it is not possible to decouple the two effects. Indeed, it would be very difficult to design a molecule where steric bulk is introduced without simultaneously introducing a minor change in electronic effects. However, evidence supporting a more dominant role of steric effects is revealed by control molecule 12, which has a Me substituent in a remote position. The IP value of 12 is very similar to unsubstituted 9 (Figure S1.2) whereas 10 and 11 have a significantly increased IP compared to 9. A similar steric effect is observed with bulky substituents in 2-4, relative to 1.
Figure S1.2 - Evolution of the IP and EA potentials with substitution on the donor and acceptor units for all molecules discussed.

S2. Computational Studies.

Computational Details. The ground and excited S₁ state geometries were optimized using density functional theory (DFT) or time-dependent DFT (TDDFT) within the approximation of the M062X exchange and correlation functional\textsuperscript{[S5]} and a Def2SVP basis\textsuperscript{[S6]} as implemented within the Gaussian 09 quantum chemistry package.\textsuperscript{[S7]} The ground state geometries were used to simulate the absorption spectra, and solvent effects were included using a Polarizable Continuum Model (PCM) with the dielectric constant for dichloromethane (DCM).\textsuperscript{[S8]} The S₁ geometries were used to calculate the emission energies, and here the effect of solvation was incorporated using the state-specific polarizable continuum solvation model (SS-PCM).\textsuperscript{[S8]} For molecules with more than one major conformer the absorption spectra were obtained by linear combination of the spectrum calculated for each conformer weighted a Boltzmann factor determined from their respective energies.
### S2.1 Calculated Energies for the Different Conformers.

#### Table S2.1

The relative energies, dipole moment (Debye), HOMO and LUMO energies (eV), and Boltzmann distributions of the major conformers for the 8 D-A-D molecules studied herein.

| Conformer | 1       | 2       | 3       | 4       | 5       | 6       | 7       | 8       | 9       | 10      | 11      | 12      |
|-----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Conformer | Ax.     | Eq.     | M.      | Ax.     | Eq.     | M.      | Ax.     | Eq.     | M.      | Ax.     | Eq.     | M.      |
| Rel. Energy (eV) | 0.00 | 0.15 | 0.07 | 0.00 | 0.64 | 0.33 | 0.20 | 0.16 | 0.00 | 0.00 | 0.00 | 0.00 |
| Dipole (D) | 10.73 | 4.04 | 9.07 | 10.70 | 8.40 | 10.43 | 11.05 | 4.97 | 9.75 | 10.86 | 10.83 | 10.82 |
| \( E_{\text{HOMO}} \) (eV) | -7.11 | -6.65 | -6.64 | -7.18 | -7.09 | -7.09 | -6.99 | -6.78 | -6.80 | -7.17 | -7.17 | -7.31 |
| \( E_{\text{LUMO}} \) (eV) | -1.02 | -1.49 | -1.24 | -0.99 | -1.39 | -1.17 | -0.86 | -1.38 | -1.06 | -1.00 | -0.99 | -0.98 |
| Boltzmann Weighting | 0.94 | 0.00 | 0.06 | 1.00 | 0.00 | 0.00 | 0.11 | 0.61 | 0.28 |

\(^a\) The computational simulations show that a specified conformer is not formed at all in some compounds. This is the case for compounds 2, 3, 4, 10 and 11 where only the axial form is present in the ground state, and for compounds 6 and 7 where only the equatorial form is predicted to exist, also in the ground state. Therefore no data is reported in these cases.
S2.2 Calculated IP and EA potentials.

Figure S2.2 - The HOMO and LUMO energies (in eV) calculated for the 12 compounds studied in this work. The trend is in excellent agreement with the experimental IP and EA potentials determined experimentally (Figure S2).
S2.3 Calculated Excited State Energies.

Table S2.3 - Energies (in eV) for the $S_1$ states and close lying triplet states, for the D–A–D and D–A conformers at the excited state equilibrium geometry ($S_1$). The bottom row is the energy gap (in eV) between the $S_1$ and the triplet state of the same character, which in all cases is the $T_1$. The solvent included in the SS-PCM formulism is toluene.

| Conformer | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|-----------|---|---|---|---|---|---|---|---|
| $T_1$     | 2.78 | 2.79 | 2.79 | 2.79 | 2.79 | 2.79 | 2.79 | 2.57 |
| $T_2$     | 3.28 | 3.39 | 3.39 | 3.39 | 3.39 | 3.39 | 3.39 | 2.51 |
| $S_1$     | 3.68 (0.0038) | 3.79 (0.0078) | 3.79 (0.0078) | 3.79 (0.0078) | 3.79 (0.0078) | 3.79 (0.0078) | 3.79 (0.0078) | 3.58 (0.0158) |
| $T_1$     | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 |
| $T_2$     | 3.34 | 3.38 | 3.38 | 3.38 | 3.38 | 3.38 | 3.38 | 2.95 |
| $S_1$     | 3.74 (0.0053) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.58 (0.0158) |
| $T_1$     | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 |
| $T_2$     | 3.34 | 3.38 | 3.38 | 3.38 | 3.38 | 3.38 | 3.38 | 2.95 |
| $S_1$     | 3.74 (0.0053) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.58 (0.0158) |
| $T_1$     | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 |
| $T_2$     | 3.34 | 3.38 | 3.38 | 3.38 | 3.38 | 3.38 | 3.38 | 2.95 |
| $S_1$     | 3.74 (0.0053) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.58 (0.0158) |
| $T_1$     | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 | 2.78 |
| $T_2$     | 3.34 | 3.38 | 3.38 | 3.38 | 3.38 | 3.38 | 3.38 | 2.95 |
| $S_1$     | 3.74 (0.0053) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.79 (0.0019) | 3.58 (0.0158) |

| Conformer | 9 | 10 | 11 | 12 |
|-----------|---|---|---|---|
| $T_1$     | 1.99 | 2.78 | 2.33 | 1.93 |
| $T_2$     | - | 3.50 | - | - |
| $S_1$     | 2.01 (0.0002) | 3.66 (0.0684) | 2.41 (0.0209) | 1.94 (0.0002) |
| $T_1$     | - | 0.02 | 0.08 | 0.01 |

$^a$ The computational simulations show that a specified conformer is not formed at all in the excited state of some compounds. This is the case for compound 8, that shows contributions from only axial and mixed forms, 2-4, 10, and 11 that show only contributions from the axial form, and 6, 7, 9 and 12 that show contributions from the equatorial form only. In some cases the calculations were also not able to find higher triplet levels for specified conformers. Therefore no data is reported in these cases.
S2.4 Calculated Absorption Spectra of compounds 1-12.
S3. X-Ray Crystallography

X-ray diffraction experiments (Table S3.1) were carried out on a Bruker 3-circle D8 Venture diffractometer with a PHOTON 100 CMOS area detector, using Mo-$K_{\alpha}$ (6, 7) or Cu-$K_{\alpha}$ (8) radiation from Incoatec IµS microsources with focussing mirrors. Crystals were cooled using a Cryostream (Oxford Cryosystems) open-flow $N_2$ gas cryostat. The data were processed using APEX3 v.2016.1-0 and reflection intensities integrated using SAINT v8.38A software (Bruker AXS, 2016). 8·CDCl$_3$ was studied at Beamline I19 of Diamond Light Source (RAL) on a dual air-bearing fixed-$\chi$ diffractometer with pixel-array photon-counting Dectris Pilatus 2M detector,[S9] using undulator radiation monochromated with double-crystal Si(111). The crystal was cryo-mounted using a remote-controlled BART robot[S10] and cooled using a Cryostream $N_2$ gas cryostat. The diffraction images were converted to Bruker format using cbf_to_sfrm.py program[S11] and further processed with APEX3 and SAINT software (vide supra). The data were corrected for absorption by a semi-empirical method based on Laue equivalents and multiple scans, using SADABS program,[S12] except that of 8 (a 2-component non-merohedral crystal twinned by a 180° rotation around the $z$ axis), which was scaled using TWINABS 2012/1 program (Bruker AXS, 2008-2012). Structure 6 was solved by iterative method using olex2.solve program,[S13] 7 by direct methods using SHELXS 2013/1 program,[S14] 8 and 8·CDCl$_3$ by dual-space intrinsic phasing method using SHELXT 2018/2 program[S15], and refined by full-matrix least squares using SHELXL software[S16] on OLEX2 platform.[S17]

On cooling below 180 K, compound 7 undergoes a gradual and reversible phase transition with doubling of the $c$ parameter. The structures were determined at 190 K (RT-phase) and 120 K (LT-phase). The latter has a sublattice (corresponding to the actual lattice of the RT-phase) and contains two independent molecules of nearly the same conformations as the single one in the RT-phase.
### Table S3.1. Crystal data and experimental details

| Compound | 6 (high T) | 7 (low T) | 8 | 8 CDCl$_3$ |
|----------|------------|-----------|---|------------|
| CCDC no. | 1884010    | 1884007   | 1884011 | 1884008    |
| Formula  | C$_{38}$H$_{26}$N$_2$O$_2$S$_3$ | C$_{42}$H$_{34}$N$_2$O$_2$S$_3$ | C$_{44}$H$_{38}$N$_2$O$_2$S$_3$ | C$_{44}$H$_{38}$N$_2$O$_2$S$_3$CDCl$_3$ |
| Formula weight | 638.79 | 694.89 | 722.94 | 843.32 |
| D$_{calc}$/g cm$^{-3}$ | 1.441 | 1.360 | 1.375 | 1.325 |
| μ/mm$^{-1}$ | 0.29 | 0.26 | 0.26 | 2.19 |
| T/K | 120 | 190 | 120 | 120 |
| Radiation | Mo-K$_α$ | Mo-K$_α$ | Cu-K$_α$ | synchrotron |
| λ/Å | 0.71073 | 0.71073 | 1.54184 | 0.6889 |
| Crystal System | triclinic | triclinic | monoclinic | monoclinic |
| Space Group | P̅1 (no. 2) | P̅1 (no. 2) | P̅2$_1$/m (no. 11) |
| α/° | 79.822(3) | 77.138(2) | 76.632(3) |
| β/° | 75.146(3) | 84.451(2) | 83.723(3) |
| γ/° | 73.305(3) | 83.336(3) | 83.531(3) |
| a/Å | 8.7268(8) | 12.9638(10) | 16.766(4) |
| b/Å | 13.2586(11) | 14.1725(10) | 7.6155(19) |
| c/Å | 13.8335(12) | 9.5622(6) | 31.336(8) |
| Z | 2 | 2 | 4 | 2 |
| $θ_{max}$/° | 50 | 50 | 50 | 50 |
| Reflections total | 23441 | 23900 | 53040 | 20383 |
| unique | 5185 | 6043 | 3518 | 3922 |
| with $I > 2(I)$ | 5435 | 3903 | 3035 | 3441 |
| $R_{int}$ | 0.086 | 0.064 | 0.060 | 0.089 |
| Parameters /restraints | 409/0 | 451/6 | 451/6 | 253 |
| Δρ$_{max}$/min/eÅ$^-3$ | 0.33, -0.31 | 0.40, -0.34 | 0.44, -0.40 | 0.31, -0.33 |
| Goodness of fit | 1.014 | 1.105 | 1.028 | 1.062 |
| $R_1$, wR$_2$ (all data) | 0.093, 0.098 | 0.095, 0.113 | 0.069, 0.121 | 0.063, 0.107 |
| $R_1$, wR$_2$ [$I > 2(I)$] | 0.046, 0.084 | 0.049, 0.095 | 0.043, 0.108 | 0.049, 0.099 |

### Table S3.2. Molecular geometry of 6-8

|  | $τ_1$/° | $θ_1$/° | $τ_2$/° | $θ_2$/° | C(A)-N/Å | C(D)-N/Å |
|---|---------|---------|---------|---------|-----------|-----------|
| 6 | 66.1 | 151.3 | 86.6 | 156.5 | 1.420(3) | 1.436(6) |
| 7 (190 K) | 73.0 | 150.0 | 87.4 | 155.3 | 1.420(5) | 1.444(3) |
| 7 (120 K) | 70.6 | 148.0 | 86.4 | 155.1 | 1.422(4) | 1.440(3) |
| 8 | 58.2$^a$ | 140.4 | 80.9$^b$ | 144.0 | 1.43(1)$^a$ | 1.441(3) |
| 8·CDCl$_3$ | 67.7$^a$ | 149.0 | 74.7$^b$ | 158.4 | 1.425(8) | 1.430(5) |

$^a$ Major isomer; $^b$ minor isomer
Figure S3.1. X-ray molecular structure of 6. Thermal ellipsoids are drawn at 50% probability level, H atoms are omitted.
Figure S3.2. X-ray molecular structure of 7 at 190 K (top) and 120 K (bottom, two independent molecules). Thermal ellipsoids are drawn at 50% probability level, H atoms are omitted.
Figure S3.3. X-ray molecular structures of 8 (unsolvated form) (top) and 8·CDCl₃ (bottom) The primed atoms are generated by twofold axis and mirror plane, respectively. Thermal ellipsoids are drawn at 50% probability level, H atoms and minor conformers are omitted.
**S4. General chemistry experimental details**

All reactions were carried out under an argon atmosphere unless otherwise stated. Starting materials were purchased commercially and were used as received. Solvents were dried using an Innovative Technology solvent purification system and were stored in ampoules under argon.

TLC analysis was carried out using Merck Silica gel 60 F$_{254}$ TLC plates and spots were visualised using a TLC lamp emitting at 365 or 254 nm. Silica gel column chromatography was performed using silica gel 60 purchased from Sigma Aldrich.

$^1$H and $^{13}$C NMR spectroscopy was carried out on Bruker AV400 and Varian VNMRS 600 and 700 spectrometers. Residual solvent peaks were referenced as described in the literature$^{[S18]}$, and all NMR data was processed in MestReNova V12.
Melting points were carried out on a Stuart SMP40 machine with a ramping rate of 4 °C min⁻¹. Videos were replayed manually to determine the melting point.

High resolution mass spectrometry was carried out on a Waters LCT Premier XE using ASAP ionisation and TOF detection. Samples were analysed directly as solids. Any mention of Br in MS data refers to ⁷⁹Br isotope.

Elemental analysis was performed on an Exeter Analytical E-440 machine.

3,7-dimethyl dibenzothiophene was prepared according to a literature procedure.[S19]

2-bromodibenzo thiophene-S,S-dioxide was prepared according to a literature procedure, using 2-bromodibenzo thiophene purchased from TCI chemicals as starting material.[S20]

Molecules 1,[S21] 2–5 and 10–11,[S20] and 9[S22] were analysed using literature data and samples.

Unless otherwise specified, a mixed isomers grade hexane was used.

**Synthesis of 2,8-dibromo-3,7-dimethyl dibenzothiophene**

\[
\begin{align*}
\text{CHCl}_3, 21.5 \text{ h} & \\
\text{Br}_2 (2.1 \text{ eq.}) & \\
\end{align*}
\]

To a dry 50 mL 2-necked round-bottomed flask was added 3,7-dimethyl dibenzothiophene (1.00 g, 4.7 mmol, 1 eq.). The solid was dried under vacuum for 30 min and the flask was backfilled with argon. Dry chloroform (20 mL) was added, and the mixture was stirred to allow dissolution. The reaction was cooled to 0 °C and bromine (1.56 g/ 500 μL, 9.8 mmol, 2.1 eq.) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 21 h. The precipitate that formed was filtered and washed with cold n-hexane to give product as a white solid (1.40 g, 80% yield)

\(^1\)H NMR (400 MHz, CDCl₃) δ 8.21 (s, 2H), 7.66 (s, 2H), 2.53 (s, 6H); \(^{13}\)C\(^{\{1\}}\)H NMR (176 MHz, CDCl₃) δ 138.9, 136.7, 134.2, 125.1, 124.2, 121.7, 23.6. HRMS-ASAP-TOF⁺ m/z calculated for C\(_{14}\)H\(_{10}\)SBr\(_2\) [M⁺] 367.8869, found: 367.8836; Anal. Calc. for C\(_{14}\)H\(_{10}\)SBr\(_2\) C, 45.43; H, 2.72; N, 0.0 Found: C, 45.34; H, 2.71; N, 0.0; m.p. 226 – 228 °C.

**2,8-dibromo-3,7-dimethyl dibenzothiophene-S,S-dioxide**

\[
\begin{align*}
\text{AcOH, reflux } 2 \text{ h} & \\
\text{H}_2\text{O}_2 (aq) & \\
\end{align*}
\]

Under air
To a 250 mL round-bottomed flask equipped with a magnetic stirrer bar was added 2,8-dibromo-3,7-dimethyldibenzothiophene (1.00 g, 2.7 mmol, 1 eq.) and acetic acid (40 mL). The mixture was heated with stirring at 80 °C for 30 min to aid dissolution. H$_2$O$_2$(aq) (12 mL, 35% w/w) was then added to the mixture and was heated to 120 °C for 2 h. The reaction was allowed to cool to ambient temperature, and the precipitate was collected by filtration. The powder was washed with water (4 × 50 mL) with mixing in the sinter. The product was dried at 70 °C overnight, and was purified by silica gel column chromatography eluting with CHCl$_3$. The product was isolated as a white solid (560 mg, 54% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (s, 2H), 7.66 (s, 2H), 2.51 (s, 6H); $^{13}$C{$^1$H} NMR (176 MHz, CDCl$_3$) δ 141.3, 137.0, 131.2, 129.9, 125.6, 124.0, 23.5; HRMS-ASAP-TOF $^+$ m/z calculated for C$_{14}$H$_{10}$SBr$_2$O$_2$ [M$^+$$]$ 399.8768, found: 399.8757; Anal. Calc. for C$_{14}$H$_{10}$SBr$_2$O$_2$ C, 41.82; H, 2.51; N, 0.0 Found: C, 41.97; H, 2.53; N, 0.0; m.p decomp. > 350 °C.

3,7-dimethyldibenzothiophene-S,S-dioxide

To a 10 mL round-bottomed flask equipped with a magnetic stirrer bar was added 3,7-dimethyldibenzothiophene (100 mg, 0.47 mmol, 1 eq.) and acetic acid (2 mL). The mixture was heated at 80 °C for 30 min to aid dissolution. H$_2$O$_2$(aq.) (1 mL, 35% w/w) was added and the reaction mixture was heated to 120 °C for 2.5 h. On cooling the mixture down to room temperature a precipitate formed which was collected by filtration, and was washed with water (4 × 10 mL) with mixing in the sinter. The crude product was dried in a 100 °C oven for 2 h and was then dried under vacuum overnight. The crude product was purified by silica gel column chromatography using CH$_2$Cl$_2$ as eluent. Removal of solvent under reduced pressure gave product as a white solid. (54 mg, 47% yield).

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 8.01 (d, $J = 8.0$ Hz, 2H), 7.77 (s, 2H), 7.58 (d, $J = 8.0$ Hz, 2H), 2.43 (s, 6H); $^{13}$C{$^1$H} NMR (101 MHz, DMSO-d$_6$) δ 140.9, 137.1, 135.0, 128.4, 122.1, 122.0, 20.8; HRMS-ASAP-TOF $^+$ m/z calculated for C$_{14}$H$_{13}$SO$_2$ [M+H$^+$$]$ 245.0636, found: 245.0639.
3,7-diisopropyl dibenzothiophene

\[
\text{THF, reflux, 20 h}
\]

To a 500 mL two-necked round bottomed flask equipped with a stirrer bar and reflux condenser was added 3,7-dibromodibenzothiophene (3.45 g, 10.08 mmol, 1 eq.), Pd(dppf)Cl\_2·CH\_2Cl\_2 (0.082 g, 0.101 mmol, 0.01 eq.) and dppf (0.056 g, 0.101 mmol, 0.01 eq.). The contents were dried under vacuum for 30 min, and the flask was backfilled with argon. Dry THF (200 mL) was then added via cannula transfer, and the mixture was deoxygenated with argon bubbling for 30 min. i-PrMgCl (2 M in THF, 12.6 mL, 2.5 eq.) was then added via syringe, and the reaction was refluxed for 20 h. The reaction was allowed to cool to ambient temperature, and H\_2O (100 mL) was added. The organic layer was separated and the aqueous layer was extracted with CH\_2Cl\_2 (3 × 100 mL). The organic layers were combined and dried with magnesium sulfate and were filtered. Removal of solvent under reduced pressure gave crude material which was purified by silica gel column chromatography. The product was eluted with hexane, followed by 10% CH\_2Cl\_2/hexane (v/v) giving the product as a white solid (1.45 g, approx. 54% yield). Note: Product was approx. 90% pure by NMR and was used in the next reaction without further purification. A small pure sample for analytical purposes was obtained by slow evaporation from acetone. Any impurities present were completely removed from the bulk material in the synthesis of 2,8-dibromo-3,7-diisopropyl dibenzothiophene-SS-dioxide.

\[\text{^1H NMR (400 MHz, CDCl}_3\text{) } \delta 8.01 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 1.6 Hz, 2H), 7.30 (dd, J = 8.2, 1.6 Hz, 2H), 3.05 \text{(hept, } J = 6.9 \text{ Hz, } 2H), 1.33 \text{ (d, } J = 6.9 \text{ Hz, } 12H)\]

\[\text{^13C{^1H} NMR (101 MHz, CDCl}_3\text{) } \delta 147.6, 139.7, 133.8, 123.5, 121.2, 120.3, 34.5, 24.3. HRMS-ASAP-TOF}^+ \text{ m/z calculated for } C_{18}H_{20}S [M]^+ 268.1286, \text{ found: } 268.1291; \text{ Anal. Calc. for } C_{18}H_{18}S: \text{ C, 80.55; H, 7.51; N, 0.00 Found: C, 80.49; H, 7.49; N, 0.05; m.p. 146 – 148 °C.} \]

2,8-dibromo-3,7-diisopropyl dibenzothiophene

\[
\text{CHCl}_3, 15 h
\]

To a dry 50 mL 2-necked round-bottomed flask was added 3,7-diisopropyl dibenzothiophene (1.40 g, 5.22 mmol, 1 eq.). The solid was dried under vacuum for 30 min and the flask was backfilled with argon. Dry chloroform (25 mL) was added, and the mixture was stirred to allow dissolution. The reaction was cooled to 0 °C and bromine (1.67 g/ 534 μL, 10.45 mmol, 2.0 eq.) was added dropwise. The
reaction mixture was allowed to warm to room temperature and was stirred for 15 h. Sodium thiosulfate solution (1 M, 20 mL) was added to the reaction mixture, and the mixture was extracted with CH$_2$Cl$_2$ (3 × 25 mL). The combined organic layers were dried with magnesium sulfate and were filtered. Removal of solvent under reduced pressure gave crude product. The product was purified by recrystallisation from toluene to give a white solid (1.40 g, 63% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.21 (s, 2H), 7.71 (s, 2H), 3.49 (hept, $J$ = 6.9 Hz, 2H), 1.33 (d, $J$ = 6.9 Hz, 12H), $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) δ 146.3, 139.5, 134.1, 125.6, 121.2, 120.5, 33.3, 23.2; HRMS-ASAP-TOF $m/z$ calculated for C$_{18}$H$_{18}$SBr$_2$ [M]$^+$ 423.9496, found: 423.9498; Anal. Calc. for C$_{18}$H$_{18}$SBr$_2$ C, 50.73; H, 4.26; N, 0.0 Found: C, 50.40; H, 4.19; N, 0.0; m.p. 136 – 138 °C.

2,8-dibromo-3,7-diisopropyl-dibenzothiophene-S,S-dioxide

To a 250 mL round-bottomed flask equipped with a magnetic stirrer bar was added 2,8-dibromo-3,7-diisopropyl-dibenzothiophene (1.22 g, 2.86 mmol, 1 eq.) and acetic acid (50 mL). The mixture was heated with stirring at 80 °C for 30 min to aid dissolution. H$_2$O$_2$(aq) (12 mL, 35% wt.) was added to the mixture and was heated to 120 °C for two hours. Further H$_2$O$_2$(aq) (4 mL) was added and the reaction was refluxed for one further hour. The reaction was allowed to cool to ambient temperature, and the precipitate was collected by filtration. The powder was washed several times with water with agitation of the suspension in the sinter during each wash. The product was dried at 70 °C for two hours, and was then dried under high vacuum overnight at ambient temperature. The product was isolated as a white solid (1.00 g, 76% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 (s, 2H), 7.72 (s, 2H), 3.44 (hept, $J$ = 6.8 Hz, 2H), 1.30 (d, $J$ = 6.8 Hz, 12H). $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) δ 150.8, 137.5, 130.5, 129.6, 126.1, 120.4, 33.6, 22.6; HRMS-ASAP-TOF $m/z$ calculated for C$_{18}$H$_{17}$SBr$_2$O$_2$ [M–H]$^-$ 454.9316, found: 454.9323, Anal. Calc. for C$_{18}$H$_{17}$SBr$_2$O$_2$ C, 47.18; H, 3.96; N, 0.0 Found: C, 46.72; H, 3.93; N, 0.0; m.p 245 – 247 °C.
2,8-Bis(phenothiazin-10-yl)-3,7-dimethyldibenzothiophene-S,S-dioxide (6)

![Chemical Structure]

Pd$_2$(dba)$_3$·CHCl$_3$ (5 mol%), HP$_3$Bu$_3$BF$_4$ (10 mol%), NaO$_3$Bu (3 eq.), phenothiazine (2 eq.)

Toluene, 107 °C, 20.5 h

2,8-dibromo-3,7-dimethyldibenzothiophene-S,S-dioxide (156 mg, 0.39 mmol, 1 eq.) and phenothiazine (155 mg, 0.78 mmol, 2 eq.) were dried under vacuum for 30 min in a two-neck 100 mL round-bottomed flask fitted with a reflux condenser. The flask was back-filled with argon and dry toluene (15 mL) was added via syringe. The reaction mixture was bubbled with argon for 30 min, then Pd$_2$(dba)$_3$·CHCl$_3$ (20 mg, 19 μmol, 0.05 eq.) and HP$_3$Bu$_3$BF$_4$ (11 mg, 38 μmol, 0.1 eq.) was added and the reaction mixture was bubbled with argon for a further 30 min. NaO$_3$Bu (112 mg, 1.17 mmol, 3 eq.) was added under a high flow of argon and the reaction was then heated to 107 °C with stirring for 20.5 h. At the end of the reaction the solvent was removed under reduced pressure and the crude mixture was purified by silica gel column chromatography eluting with 50% v/v CH$_2$Cl$_2$/hexane switching to 80% CH$_2$Cl$_2$/hexane. Removal of solvent under reduced pressure gave product as a yellow solid (198 mg, 80% yield). The product can be sublimed by heating (>350 °C) under high vacuum (9 × 10$^{-2}$ mbar). Crystals suitable for X-ray diffraction were obtained by slow evaporation from CD$_2$Cl$_2$.

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 8.45 (s, 2H), 8.29 (s, 2H), 7.05 (dd, $J = 7.5$, 1.6 Hz, 4H), 6.92 (ddd, $J = 8.2$, 7.4, 1.6 Hz, 4H), 6.84 (td, $J = 7.4$, 1.2 Hz, 4H), 6.11 (dd, $J = 8.2$, 1.2 Hz, 4H), 2.27 (s, 6H), $^{13}$C$[^1$H$]$ NMR (151 MHz, DMSO-d$_6$) δ 144.2, 142.0, 141.4, 137.0, 131.4, 127.8, 127.0, 126.7, 125.8, 123.0, 118.6, 115.2, 17.5; HRMS-ASAP-TOF $m/z$ calculated for C$_{38}$H$_{26}$N$_2$O$_2$S$_3$ [M]$^+$ 638.1156, found: 638.1140; Anal. Calc. for C$_{38}$H$_{26}$N$_2$O$_2$S$_3$ C, 71.45; H, 4.10; N, 4.39 Found: C, 71.63; H, 4.06; N, 4.41; m.p decomp. > 350 °C.
2,8-Bis(phenothiazin-10-yl)-3,7-isopropyldibenzothiophene-S,S-dioxide (7)

![Chemical Structure](image)

2,8-dibromo-3,7-diisopropyldibenzothiophene-S,S-dioxide (180 mg, 0.39 mmol, 1 eq.) and phenothiazine (156 mg, 0.79 mmol, 2 eq.) were dried under vacuum for 30 min in a two-neck 100 mL round-bottomed flask fitted with a reflux condenser. The flask was back-filled with argon and dry toluene (10 mL) was added \textit{via} syringe. The reaction mixture was bubbled with argon for 30 min, then \( \text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3 \) (20 mg, 19 \( \mu \)mol, 0.05 eq.) and \( \text{HPtBu}_3\text{BF}_4 \) (11 mg, 38 \( \mu \)mol, 0.1 eq.) was added and the reaction mixture was bubbled with argon for a further 30 min. \( \text{NaO}_\text{tBu} \) (112 mg, 1.17 mmol, 3 eq.) was added under a high flow of argon and the reaction was then heated to 107 °C with stirring for 20 h. At the end of the reaction the solvent was removed under reduced pressure and the crude mixture was purified by silica gel column chromatography eluting with 50\% v/v CH\(_2\)Cl\(_2\)/hexane switching to 70\% CH\(_2\)Cl\(_2\)/hexane. Removal of solvent under reduced pressure gave product as a yellow solid (150 mg, 55\% yield). Crystals suitable for X-ray diffraction were obtained by layering with CH\(_2\)Cl\(_2\)/n-hexane.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 8.10 \) (s, 2H), 7.71 (s, 2H), 7.02 – 6.92 (m, 4H), 6.87 – 6.75 (m, 8H), 6.08 – 5.98 (m, 4H), 3.45 (hept, \( J = 6.9 \) Hz, 2H), 1.18 (d, \( J = 6.9 \) Hz, 12H), \(^{13}\)C \(^1\)H NMR (151 MHz, CDCl\(_3\)) \( \delta 153.1, 143.8, 142.7, 138.3, 130.9, 127.1, 127.0, 126.1, 123.1, 123.0, 119.6, 115.3, 28.7, 23.6; \) HRMS-ASAP-TOF\(^+\) \text{m/z} \text{calculated for} \text{C}_{42}\text{H}_{34}\text{N}_2\text{O}_2\text{S}_3 [M]^+ 694.1782, \text{found:} 694.1770; \text{Anal. Calc. for} \text{C}_{42}\text{H}_{34}\text{N}_2\text{O}_2\text{S}_3 \text{Calc with 2 wt.% CH}_2\text{Cl}_2, 71.42; \text{H, 4.88; N, 3.94 Found: C, 71.64; H, 5.02; N, 3.80; m.p decomp. > 350 °C.}
2,8-Bis(1-methylphenothiazin-10-yl)-3,7-diisopropyl dibenzothiophene-S,S-dioxide (8)

2,8-dibromo-3,7-diisopropyl dibenzothiophene-S,S-dioxide (200 mg, 0.44 mmol, 1 eq.) and 1-methylphenothiazine (186 mg, 0.873 mmol, 2 eq.) were dried under vacuum for 30 min in a two-neck 100 mL round-bottomed flask fitted with a reflux condenser. The flask was back-filled with argon and dry toluene (10 mL) was added via syringe. The reaction mixture was bubbled with argon for 30 min, then Pd\(_2\)(dba)\(_3\)·CHCl\(_3\) (23 mg, 22 μmol, 0.05 eq.) and HPtBu\(_3\)BF\(_4\) (13 mg, 45 μmol, 0.1 eq.) was added and the reaction mixture was bubbled with argon for a further 30 min. NaOtBu (126 mg, 1.31 mmol, 3 eq.) was added under a high flow of argon and the reaction was then heated to 107 °C with stirring for 18 h. At the end of the reaction the solvent was removed under reduced pressure and the crude mixture was purified by silica gel column chromatography eluting with 40–70% CH\(_2\)Cl\(_2\) /hexane (v/v) in 10% increasing increments. Removal of solvent under reduced pressure gave a yellow powder, which was suspended in ethanol and boiled while toluene was added dropwise. Little dissolution was observed and the mixture was hot filtered giving a purer filtrand (NOT filtrate). This filtrand was purified by silica gel column chromatography eluting with 40% v/v CH\(_2\)Cl\(_2\) /hexane to give a yellow solid (60 mg, 19% yield). Crystals suitable for X-ray analysis were obtained by layering of either CH\(_3\)CN or butan-1-ol on top of a solution of 8 in CDCl\(_3\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.19 (s, 2H), 7.81 (s, 2H), 7.45 (dd, \(J = 8.3, 1.2\) Hz, 2H), 7.22 (dd, \(J = 7.6, 1.6\) Hz, 2H), 7.18 – 7.10 (m, 4H), 7.04 (td, \(J = 7.6, 1.2\) Hz, 2H), 7.00 (t, \(J = 7.6\) Hz, 2H), 6.95 – 6.90 (m, 2H), 4.09 (apr. p, \(J = 6.8\) Hz, 2H), 1.98 (s, 6H), 1.03 (d, \(J = 6.8\) Hz, 12H), \(^{13}\)C\{\(^1\)H\} NMR (176 MHz, CDCl\(_3\)) \(\delta\) 151.0, 149.3, 144.7, 143.1, 136.3, 132.1, 131.3, 131.1, 129.3, 129.1, 127.9, 127.3, 125.9, 125.7, 125.5, 125.0, 122.0, 121.5, 28.8, 23.9, 21.7; HRMS-ASAP-TOF \(m/z\) calculated for C\(_{44}\)H\(_{39}\)N\(_2\)O\(_2\)S\(_3\) [MH\(^+\)] \(723.2174\), found: 723.2173, Anal. Calc. for C\(_{44}\)H\(_{38}\)N\(_2\)O\(_2\)S\(_3\), 73.10; H, 5.30; N, 3.87 Found: C, 72.99; H, 5.34; N, 3.80; m.p decomp. > 350 °C.
This synthesis was based on a modified literature procedure.\[S23\]

To a 50 mL two-neck round-bottomed flask equipped with a stirrer bar and reflux condenser was added N-(4-methylphenyl)aniline (2.00 g, 10.9 mmol, 1 eq.). The amine was dried under vacuum for 30 min, and the setup was backfilled with argon. Under a flow of argon was added sulfur (699 mg, 21.8 mmol, 2 eq.) and I\(_2\) (83 mg, 0.327 mmol, 0.03 eq.) and anhydrous 1,2-dichlorobenzene (4 mL). The reaction mixture was then deoxygenated by bubbling with argon for 30 min, and was then heated using a drysyn\textsuperscript{TM} kit set to 160 °C for 45 min. After the reaction mixture cooled to room temperature, saturated sodium thiosulfate\(_{aq}\) (10 ml) was added followed by \(\text{H}_2\text{O}\) (20 ml). The reaction mixture was extracted with \(\text{CH}_2\text{Cl}_2\) (3 × 100 ml). The organic layer was dried with MgSO\(_4\) and was filtered. Removal of solvent under reduced pressure gave crude product. The crude mixture was purified by silica gel column chromatography eluting with \(\text{CH}_2\text{Cl}_2\):hexane (gradient: pure hexane → 20% \(\text{CH}_2\text{Cl}_2\):hexane (v/v)). Removal of solvent under reduced pressure gave product as a yellow solid which was recrystallised from hot hexane with slow addition of acetone until dissolution was achieved. Filtration gave high purity product as a yellow crystalline solid (320 mg, 14% yield). Note: The reaction must not be over heated due to loss of a methyl group from the product. Phenothiazine is inseparable from the product here and in subsequent reactions. Note: More product was obtained with approx. 90% purity (650 mg, 28%), however high purity material was imperative for the next step.

Data matches exactly as previously reported in the literature\[S24\].
2-(3-methylphenothiazin-10-yl)-dibenzothiophene-S,S-dioxide (12)

![Chemical structure](image)

2-Bromodibenzothiophene-S,S-dioxide (261 mg, 0.88 mmol, 1 eq) and 3-methylphenothiazine (189 mg, 0.88 mmol, 1 eq) were dried under vacuum in a 2-neck 100 mL round bottomed flask equipped with a reflux condenser. The flask was backfilled with argon and anhydrous toluene (15 mL) was added via syringe. The solution was deoxygenated by bubbling with argon for 15 min. Pd$_2$(dba)$_3$·CHCl$_3$ (46 mg, 44 μmol, 0.05 eq.) and HPBu$_3$BF$_4$ (26 mg, 0.89 μmol, 0.1 eq.) were added and the solution was bubbled with argon for a further 15 min. NaOtBu (170 mg, 1.77 mmol, 2.0 eq.) were added and the mixture heated at 110 °C under argon for 18 h. Upon cooling to ambient temperature, water (50 mL) was added and products were extracted in to CH$_2$Cl$_2$ (3 × 70 mL). The organic layer was dried over magnesium sulfate and the solvent removed under reduced pressure to give the crude product. The crude product was purified by silica gel column chromatography eluting with CH$_2$Cl$_2$. The solvent was removed under reduced pressure and gave pure product as a yellow solid (120 mg, 32% yield). The product can be sublimed by heating (>210 °C) under high vacuum (5 × 10$^{-2}$ mbar). Note: Fractions should be analysed individually to obtain product of the best purity. TLC analysis showed column fractions containing only one spot but not all fractions were the same purity. The yield reflects only pure fractions.

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 8.01 (dt, $J = 7.7, 0.9$ Hz, 1H), 7.98 – 7.94 (m, 2H), 7.81 (d, $J = 2.0$ Hz, 1H), 7.75 (td, $J = 7.6, 1.1$ Hz, 1H), 7.65 (td, $J = 7.6, 1.0$ Hz, 1H), 7.43 (dd, $J = 7.7, 1.5$ Hz, 1H), 7.32 – 7.23 (m, 3H), 7.18 (td, $J = 7.5, 1.3$ Hz, 1H), 7.13 – 7.07 (m, 2H), 7.01 (d, $J = 8.2$ Hz, 1H), 2.28 (s, 3H); $^{13}$C{$^1$H} NMR (151 MHz, DMSO-d$_6$) δ 149.0, 141.4, 138.8, 137.8, 135.0, 134.3, 133.4, 131.3, 131.2, 130.2, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 125.4, 124.0, 123.1, 122.9, 122.7, 122.6, 121.8, 113.9, 20.1; HRMS-ASAP-TOF$^+$ $m/z$ calculated for C$_{25}$H$_{18}$NO$_2$S$_2$ [MH]$^+$ 428.0779, found: 428.0763; Anal. Calc. for C$_{25}$H$_{17}$NO$_2$S$_2$: C, 70.23; H, 4.01; N, 3.28. Found: C, 70.19; H, 3.99, N, 3.23. m.p 210 – 212 °C.
$^1$H and $^{13}$C($^1$H) NMR spectra
Analytical sample from slow evaporation with acetone

Bulk Sample from Column
**Spectroscopy and photophysics.** Thin films in zeonex were prepared by spin coating with guest:zeonex ratio of (1:20 w/w) from toluene solutions. Absorption and emission spectra were collected using a UV-3600 double beam spectrophotometer (Shimadzu), and a Fluorolog fluorescence spectrometer (Jobin Yvon). The extinction coefficient determination was performed in DCM solution. Phosphorescence, prompt fluorescence (PF), and delayed emission (DF) spectra and decays were recorded using nanosecond gated luminescence and lifetime measurements with either a high energy pulsed Nd:YAG laser emitting at 355 nm (EKSPLA) with pulse width $\approx 170$ ps. Emission was focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics) having sub-nanosecond resolution. PF/DF time resolved measurements were performed by exponentially increasing the gate and delay times. In general, time gated acquisition of luminescence signals is performed using increasing delay times, while the integration time is kept constant. The disadvantage in this method is that for weak signals, no luminescence can be measured at long-delay times with good S/N ratio. An alternative to this approach is to use increasing delay and integration times, so weak signals can be measured with good S/N ratio, as the integration time increases with delay time. The delay and integration times are chosen in a way that the next delay is set at a time longer than the previous delay+integration time. Therefore, no spectral overlap exists between the spectra corresponding to successive delays. The curve obtained directly from this process does not represent the real luminescence decay. However, this is easily corrected by integrating the measured spectra and dividing the integral by the corresponding integration time. In this way, each experimental point represents a snap-shot of the number of photons emitted per second at a time $t=delay+(integration\ time)/2$. The luminescence decay is then obtained by plotting each experimental point against time, and fitting with sum of exponentials. When required. In this way we are able to collect luminescence decaying over 8 decades in time and in a single experiment. For initial development of these methods see previously published literature.

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