Supporting Information

Controlling Ultralong Room Temperature Phosphorescence in Organic Compounds with Sulfur Oxidation State

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General

Solvents used were reagent grade and used without any further purification. HPLC grade solvents were used for analyses. 9-H carbazole was purchased from Sigma-Aldrich (China) and was crystallized from toluene solution before use. Other purchased chemicals were used without further purification. Bis(4-bromophenyl)sulfane was synthesized following the literature procedure.¹

Spectroscopy

¹H, ¹³C{¹H}, COSY, NOESY, HSQC and HMBC NMR experiments were collected using a Bruker AV-400 spectrometer and referenced first to TMS and then to the residual protonated solvent peak. NMR solvents (Aldrich or Cambridge Isotope Laboratories) were used as received. Electrospray ionization mass spectrometry data were obtained using a Bruker Esquire LC ion trap mass spectrometer. Infrared spectroscopy was performed on an attenuated total reflection (ATR) crystal using a Perkin-Elmer Frontier FT-IR spectrometer. UV-vis absorption spectra were recorded on a Varian-Cary 5000 UV-Vis-near-IR spectrophotometer. Steady-state photoluminescence data were collected using a Photon Technology International (PTI) QuantaMaster 50 fluorimeter fitted with an integrating sphere, double excitation monochromator and utilizing a 75 W Xe arc lamp as the source. Fluorescence and phosphorescence lifetime data were collected using a Horiba Yvon Fluorocube TCSPC apparatus with a 370 nm NanoLED (fluorescence) or a 359 nm Horiba spectral LED (phosphorescence). The photoluminescence lifetime data were fitted using the DAS6 Data Analysis software package. Time-resolved photoluminescence spectra utilizing a 1 ms delay were measured using a Photon Technology International (PTI) QuantaMaster 400 equipped with a 359 nm Horiba spectral LED. Time-resolved spectra ranging from microsecond to 110
ms were measured using the same spectrometer coupled with a 320 nm Ng:YAG laser. Samples for low-temperature spectroscopy and lifetime measurements were cooled using an Oxford Instruments Optistat DN coupled with an ITC601 temperature controller.

X-Ray Diffraction

Single-crystal X-ray data were collected using a Bruker APEX DUO diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 K. Raw frame data were processed using APEX2. The program SAINT+, v.7.68 was used to reduce the data and the program SADABS was used to make corrections to the empirical absorptions. Space group assignments were made using XPREP on all compounds. In all cases, the structures were solved in the Olex2 suite\(^2\) of programs using Intrinsic Phasing and refined using full-matrix least-squares/difference Fourier techniques on F2 using SHELXL.\(^3\) Diagrams and publication material were generated using CrystalMaker. Powder X-ray crystallography data were collected on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation.

Photophysical Data
Figure S1. Normalized absorption spectra of (a) CBZ-S, (c) CBZ-SO and (e) Cbz CBZ-SO₂. Normalized photoluminescence spectra of (b) CBZ-S, (d) CBZ-SO and (f) CBZ-SO₂. (λ_{ex} = 320 nm). All spectra were recorded in ~ 2 × 10^{-5} M cyclohexanes (CH₆), dichloromethane (CH₂Cl₂) and acetonitrile (MeCN) solutions at room temperature.

RTP Arbitrary Efficiency $\Phi$:

$$\Phi = \frac{\Phi_F}{\Phi_A}$$

$A_F$: Integration of phosphorescence peak
$A_F$: Integration of fluorescence peak
$\Phi_F$: fluorescence quantum yield.
**Figure S2.** Fluorescence decay profile of CBZ-S, CBZ-SO and CBZ-SO$_2$ in the crystalline state.

**Table S1.** Summary of solid state photophysical data

|       | PLQY | Fluorescence | Phosphorescence (Air)$^{[b]}$ | Phosphorescence (77K)$^{[b]}$ |
|-------|------|--------------|-------------------------------|-------------------------------|
|       | $\lambda_{em}$ (nm)$^{[a]}$ | $\lambda_{em}$ (nm) | $\tau$ (ms)$^{[c]}$ | $\tau_{avg}$ (ms)$^{[d]}$ | $\tau$ (ms)$^{[c]}$ | $\tau_{avg}$ (ms)$^{[d]}$ |
| CBZ-S | 0.27 | 390          | 565                          | 169.13 (0.48), 226.97        | 777.19 (0.54), 1033.1 |
|       |      |              |                              | 373.46 (0.15)                | 1657.3 (0.16)          |
| CBZ-SO| 0.21 | 388          | 565                          | 114.92 (0.55), 291.24        | 808.92 (0.51), 1395.1  |
|       |      |              |                              | 445.02 (0.19)                | 1877.4 (0.32)          |
| CBZ-SO$_2$| 0.75 | 388          | 562                          | 98.87 (0.58), 309.46         | 1173.8(0.62), 1798.7   |
|       |      |              |                              | 471.37 (0.18)                | 2461.8 (0.30)          |

$^{[a]}$ Inset.$^{[b]}$ Inset.$^{[c]}$ Inset.$^{[d]}$ Inset.
Figure S3. Powder X-ray diffraction (pXRD) patterns of CBZ-S crystalline powder (black) compared to their single crystal simulated patterns (red).
Figure S4. Powder X-ray diffraction (pXRD) patterns of CBZ-SO crystalline powder (black) compared to their single crystal simulated patterns (red).

**Synthetic Details**

Scheme S1. Synthetic route of CBZ-S, CBZ-SO and CBZ-SO₂.
**CBZ-S**

This compound has been previously synthesized.\(^4\) Bis(4-bromophenyl)sulfane (344 mg, 1.0 mmol, 1.0 equiv.), 9H-Carbazole (334 mg, 2.0 mmol, 2.0 equiv.), Cs\(_2\)CO\(_3\) (650 mg, 2.0 mmol, 2.0 equiv.), Cul (38 mg, 0.2 mmol, 0.2 equiv.) and DMF (2 mL) were added to a 5-mL vial. The vial was sealed and placed in a Biotage microwave cavity. After irradiation at 220 °C for 80 minutes, the reaction mixture was poured into water (25 mL) and extracted with CH\(_2\)Cl\(_2\) (3 × 15 mL). The organic layers were combined and dried over anhydrous MgSO\(_4\), filtered, and concentrated under vacuum. Purification by column chromatography (1:30 EtOAc: hexanes) gave the pure product as a white solid (300 mg, 0.58 mmol, 58%).

\(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz): \(\delta = 8.16\) (H\(_9\), d, \(J = 7.7\) Hz, 4 H), 7.71 (H\(_2\), d, \(J = 8.5\) Hz, 4 H), 7.61 (H\(_3\),d, \(J = 8.5\) Hz, 4 H), 7.48 (d, \(J = 7.3\) Hz, 4 H), 7.43(t, \(J = 7.5\) Hz, 4 H), 7.30 (H\(_8\), t, 7.3 Hz, 4 H). \(^{13}\)C\{\(^1\)H\} NMR (CD\(_2\)Cl\(_2\), 101 MHz): \(\delta = 141.3\) (C\(_5\)), 137.5 (C\(_4\)), 135.1 (C\(_1\)), 133.12 (C\(_2\)), 128.4 (C\(_3\)), 126.6 (C\(_7\)), 124.0 (C\(_{10}\)), 120.8 (C\(_9\)), 120.7 (C\(_8\)), 110.3 (C\(_6\)). HRMS: calculated m/z: 516.1660, found (EI) m/z: 516.1658 [M]\(^+\).

**CBZ-SO**

To a solution of \textbf{CBZ-S} (0.103 g, 0.20 mmol, 1.0 equiv.) in CH\(_2\)Cl\(_2\) (10 mL) at 0 °C was added 70% \textit{m}-chloroperoxybenzoic acid (\textit{m}-CPBA, 0.050 g, 0.20 mmol, 1.0 equiv.) and the mixture was stirred for 0.5 h. The reaction mixture was poured into a saturated aqueous solution of sodium bicarbonate (15 mL) and was then extracted with CH\(_2\)Cl\(_2\) (3 × 10 mL). The organic layers were combined, dried over anhydrous MgSO\(_4\), filtered, and concentrated under vacuum. Purification by column chromatography (CH\(_2\)Cl\(_2\)) gave the pure product as a white solid (0.080 g, 0.15 mmol, 75%). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz): \(\delta = 8.15\) (H\(_6\), d, \(J = 7.7\) Hz, 4 H), 8.01 (H\(_2\), d, \(J = 7.7\) Hz, 4 H), 7.80 (H\(_3\), d, \(J = 7.8\) Hz, 4 H), 7.49 (H\(_6\),d, \(J = 8.1\) Hz, 4 H), 7.43 (H\(_7\), t, \(J = 7.6\) Hz, 4 H), 7.31 (H\(_8\), t, \(J = 7.4\) Hz, 4 H). \(^{13}\)C\{\(^1\)H\} NMR (CD\(_2\)Cl\(_2\), 101 MHz): \(\delta = 144.9\) (C\(_1\)), 141.1 (C\(_4\)), 141.0 (C\(_3\)), 128.3 (C\(_5\)), 127.1 (C\(_2\)), 126.8 (C\(_7\)), 124.3 (C\(_{10}\)), 121.1 (C\(_6\)), 120.9 (C\(_9\)).
To a solution of CBZ-S (0.103 g, 0.20 mmol) in CH₂Cl₂ (4 mL) at 0 °C was added 70% m-chloroperoxybenzoic acid (m-CPBA, 0.108 g, 0.44 mmol, 2.2 equiv.) and the mixture was stirred for 1 hour. The reaction mixture was poured over a saturated aqueous solution of sodium bicarbonate (20 mL) and extracted with CH₂Cl₂ (3 × 15 mL). The organic layers were combined, dried over anhydrous MgSO₄, filtered, and concentrated under vacuum. The crude material was purified by column chromatography (2:1 hexanes: CH₂Cl₂) to afford the pure product as a white solid (93 mg, 0.17 mmol, 85%). 

\[ \delta = 8.28 (H_2, d, J = 8.6 \text{ Hz}, 4 \text{ H}), 8.15 (H_9, d, J = 7.7 \text{ Hz}, 4 \text{ H}), 7.85 (H_3, d, J = 8.6 \text{ Hz}, 4 \text{ H}), 7.52 (H_6, d, J = 8.2 \text{ Hz}, 4 \text{ H}), 7.43 (H_7, t, J = 7.7 \text{ Hz}, 4 \text{ H}), 7.33 (H_8, t, J = 7.5 \text{ Hz}, 4 \text{ H}) \].

\[ \delta_{13C} (\text{H}) \text{ NMR (CD₂Cl₂, 101 MHz): } 143.2 (C_4), 140.6 (C_5), 140.1 (C_1), 130.3 (C_2), 127.8 (C_3), 126.9 (C_7), 124.7 (C_{10}), 121.5 (C_8), 120.0 (C_9), 110.2 (C_6). \]

IR (neat): (σ (SO)) 1154 and 1313 cm⁻¹.
Figure S5. $^1$H NMR spectra of CBZ-S in CD$_2$Cl$_2$ at 25 °C.

Figure S6. $^{13}$C{$^1$H} NMR spectra of CBZ-S in CD$_2$Cl$_2$ at 25 °C.
Figure S7. $^1$H NMR spectra of CBZ-SO in CD$_2$Cl$_2$ at 25 °C.

Figure S8. $^{13}$C{$^1$H} NMR spectra of CBZ-SO in CD$_2$Cl$_2$ at 25 °C.
Figure S9. $^1$H NMR spectra of CBZ-SO$_2$ in CD$_2$Cl$_2$ at 25 °C.

Figure S10. $^{13}$C$_{^1}$H NMR spectra of CBZ-SO$_2$ in CD$_2$Cl$_2$ at 25 °C.
**Computational Details**

Molecular geometries have been optimized within the density functional theory (DFT) with the ωB97X-D exchange-correlation functional and the 6-31+G(d) atomic basis set. Electronic transitions to the lowest singlet and triplet states and the interstate (singlet-triplet) spin-orbit couplings have been computed with the time-dependent version of DFT (TDDFT), and with the same energy functional and basis set. All calculations have been done with the Q-Chem package.

**Table S2.** Bond angles C-S-C and C-S-O, and dihedral angles Ph-CBZ, Ph-Ph and CBZ-CBZ (in degrees) for the crystal and optimized molecular structures of the CBZ-SO$_n$ dimers. C-S-O angles in CBZ-SO$_2$ correspond to average values.

| angle     | crystal  | optimized |
|-----------|----------|-----------|
|           | CBZ-S    | CBZ-SO    | CBZ-SO$_2$ | CBZ-S    | CBZ-SO    | CBZ-SO$_2$ |
| C-S-C     | 104.8    | 100.3     | 106.2      | 101.8    | 95.8      | 103.2      |
| C-S-O     | -        | 103.9     | 107.8      | -        | 106.5     | 107.6      |
| Ph-CBZ    | 118.5    | 125.4     | 123.6      | 122.2    | 123.5     | 125.6      |
| Ph-Ph     | 82.5     | 69.1      | 70.2       | 66.6     | 9.9       | 2.6        |
| CBZ-CBZ   | 2.1      | 4.1       | 4.1        | 23.5     | 77.7      | 93.1       |

**Table S3.** Vertical excitation energies (in eV), oscillator strengths ($f$ in parenthesis) and electronic character to the lowest singlet and triplet states of the 9-phenylcarbazole molecule computed at the ground state optimized geometry at the ωB97X-D/6-31+G(d) level. CBZ/Ph = local excitation on carbazole/phenyl; CT = CBZ→Ph charge transfer.

| state | ΔE ($f$) | character       |
|-------|----------|-----------------|
| $T_1$ | 3.25     | CBZ (B$_2$)     |
| $T_2$ | 3.56     | CBZ (A$_1$)     |
| $T_3$ | 3.66     | Ph; CT          |
| $S_1$ | 4.38 (0.050) | CBZ (A$_1$); CT |
| $S_2$ | 4.82 (0.164) | CBZ (B$_2$)     |
| $S_3$ | 4.91 (0.156) | CT              |
Table S4. Vertical excitation energies (in eV), oscillator strengths \( f \) in parenthesis, electronic character, and orbital contributions (in %) to the lowest singlet and triplet states of the CBZ-SO\(_n\) dimers computed at the ground state optimized geometries at the \( \omega B97X-D/6-31+G(d) \) level. CBZ/Ph = local excitation on carbazole/phenyl; CT = CBZ\( \rightarrow \)Ph charge transfer; n(S): lone-pairs of S atom. H = HOMO; L = LUMO.

| state \( \Delta E (f) \) | character | \% contribution |
|-------------------------|-----------|-----------------|
| CBZ-S                   |           |                 |
| T\(_1\) 3.24            | CBZ       | 16,16 H-2\( \rightarrow \)L+1,L+2; 15,15 H-3\( \rightarrow \)L+1,L+2 |
| T\(_2\) 3.24            | CBZ       | 16,16 H-3\( \rightarrow \)L+1,L+2; 15,15 H-2\( \rightarrow \)L+1,L+2 |
| T\(_3\) 3.35            | Ph; CT; n(S)\( \rightarrow \)Ph | 29,24 H,H-4\( \rightarrow \)L; 9 H-7\( \rightarrow \)L+3 |
| T\(_4\) 3.42            | Ph; CT; n(S)\( \rightarrow \)Ph | 22,18 H,H-4\( \rightarrow \)L+4; 12,10 H-8,H-1\( \rightarrow \)L |
| S\(_1\) 4.38 (0.219)    | CBZ; n(S)\( \rightarrow \)CZ | 38 H\( \rightarrow \)L+1; 38 H-1\( \rightarrow \)L+2 |
| S\(_2\) 4.39 (0.034)    | CBZ; n(S)\( \rightarrow \)CZ | 42 H-1\( \rightarrow \)L+1; 40 H\( \rightarrow \)L+2 |
| S\(_3\) 4.47 (0.486)    | CT; n(S)\( \rightarrow \)Ph | 59 H\( \rightarrow \)L; 15 H-1\( \rightarrow \)L+4; 11 H-4\( \rightarrow \)L |
| CBZ-SO                  |           |                 |
| T\(_1\) 3.24            | CBZ       | 57 H-2\( \rightarrow \)L+3; 7 H\( \rightarrow \)L+8 |
| T\(_2\) 3.24            | CBZ       | 57 H-3\( \rightarrow \)L+2; 9 H-1\( \rightarrow \)L+7 |
| T\(_3\) 3.47            | Ph; CT    | 23,16 H-7,H\( \rightarrow \)L; 8 H-8\( \rightarrow \)L+1 |
| T\(_4\) 3.51            | Ph; CT; n(S,O)\( \rightarrow \)Ph | 13,10 H-1,H-4\( \rightarrow \)L; 10,10 H,H-7\( \rightarrow \)L+4 |
| S\(_1\) 4.40 (0.163)    | CBZ       | 40 H\( \rightarrow \)L+3; 20,12 H-1\( \rightarrow \)L+2,L+3 |
| S\(_2\) 4.41 (0.051)    | CBZ       | 44,9 H-1,H\( \rightarrow \)L+2; 26 H\( \rightarrow \)L+3 |
| S\(_3\) 4.48 (0.331)    | CT        | 47 H\( \rightarrow \)L; 17,11 H-1\( \rightarrow \)L+4,L; 12 H-6\( \rightarrow \)L+4 |
| CBZ-SO\(_2\)            |           |                 |
| T\(_1\) 3.24            | CBZ       | 31 H-3\( \rightarrow \)L+3; 31 H-2\( \rightarrow \)L+2 |
| T\(_2\) 3.24            | CBZ       | 31 H-3\( \rightarrow \)L+2; 31 H-2\( \rightarrow \)L+3 |
| T\(_3\) 3.37            | Ph; CT    | 30,26 H,H-2\( \rightarrow \)L; 10 H-1\( \rightarrow \)L+4 |
| T\(_4\) 3.51            | Ph; CT    | 21 H-1\( \rightarrow \)L; 17 H\( \rightarrow \)L+4 |
| S\(_1\) 4.27 (0.511)    | CT        | 68 H\( \rightarrow \)L; 22 H-1\( \rightarrow \)L+4 |
| S\(_2\) 4.42 (0.174)    | mainly CT; CBZ | 43,13 H-1\( \rightarrow \)L,L+2; 19,13 H\( \rightarrow \)L+4,L+3 |
| S\(_3\) 4.43 (0.026)    | CBZ       | 42 H\( \rightarrow \)L+2; 41 H-1\( \rightarrow \)L+3 |
Figure S11. Main orbital contributions to the S\textsubscript{1} excitation of CBZ-SO\textsubscript{n} at the Franck-Condon geometry computed at the ωB97X-D/6-31+G(d) level. Note: the LUMO of CBZ-SO\textsubscript{2} shows overlap of π-orbitals of the two carbons bonded to S (but no contributions from S orbitals). The weight of O atomic orbitals in the LUMO is very small.

Figure S12. Crystal (top) and optimized (bottom) molecular structures of CBZ-SO and CBZ-SO\textsubscript{2} dimers. Short SO···H contacts (dashed lines) indicated in Angstroms.
Table S5. Vertical deexcitation energies (in eV), oscillator strengths ($f$ in parenthesis) and electronic character from the optimized singlet and triplet excited state potential energy surface of the \textit{CBZ-SO$_n$} dimers computed at the $\omega$B97X-D/6-31+G(d) level. $S_{\text{loc}}$ = localized singlet, $S_{\text{deloc}}$ = delocalized singlet, $S_{\text{ex}}$ = excimer-like, $T_1$ = local triplet.

| molecule | state | $\Delta E$ ($f$) |
|----------|-------|------------------|
| CBZ-S    | $S_{\text{loc}}$ | 4.13 (0.086)     |
|          | $S_{\text{deloc}}$ | 3.85 (0.569)    |
|          | $T_1$           | 2.47             |
| CBZ-SO   | $S_{\text{loc}}$ | 4.17 (0.084)     |
|          | $S_{\text{ex}}$ | 3.64 (0.075)     |
|          | $T_1$           | 2.47             |
| CBZ-SO$_2$ | $S_{\text{ex}}$ | 3.50 (0.060)     |
|          | $T_1$           | 2.47             |

Figure S13. Main orbital contributions to the local ($S_{\text{loc}}$, left) and delocalized ($S_{\text{deloc}}$, right) excited state minima of \textit{CBZ-S} computed at the $\omega$B97X-D/6-31+G(d) level.
**Figure S14.** Main orbital contributions to the local ($S_{loc}$, left) and excimer-like ($S_{ex}$, right) excited state minima of CBZ-SO computed at the ωB97X-D/6-31+G(d) level.

**Figure S15.** Main orbital contributions to the excimer-like ($S_{ex}$) state minimum of CBZ-SO$_2$ computed at the ωB97X-D/6-31+G(d) level.

**Figure S16.** Main orbital contributions to the lowest triplet ($T_1$) state minimum of CBZ-SO$_n$ computed at the ωB97X-D/6-31+G(d) level.
**Figure S17.** Excited state ($S_{ex}$) optimized geometry and crystal molecular structure of CBZ-SO$_2$.

**Table S6.** Vertical excitation energies (in eV), oscillator strengths ($f$ in parenthesis) and electronic character to the lowest singlet and triplet states of the CBZ-SO$_n$ dimers for the crystal molecular geometries computed at the ωB97X-D/6-31+G(d) level. CBZ/Ph = local excitation on carbazole/phenyl; CT = CBZ→Ph charge transfer.

| state | CBZ-S | CBZ-SO | CBZ-SO$_2$ | character    |
|-------|-------|--------|------------|--------------|
| $T_1$ | 3.21  | 3.20   | 3.27       | CBZ; CT      |
| $T_2$ | 3.21  | 3.21   | 3.27       | CBZ; CT      |
| $T_3$ | 3.37$^a$ | 3.42 | 3.52       | CBZ; Ph; CT  |
| $T_4$ | 3.48$^a$ | 3.48 | 3.53       | CBZ; Ph; CT  |
| $S_1$ | 4.34 (0.306)$^a$ | 4.35 (0.507)$^a$ | 4.44 (0.490)$^b$ | CBZ; Ph; CT |
| $S_2$ | 4.37 (0.068)$^a$ | 4.41 (0.089) | 4.48 (0.115) | CBZ; Ph; CT |
| $S_3$ | 4.48 (0.487)$^a$ | 4.45 (0.013)$^a$ | 4.55 (0.200) | CBZ; Ph; CT |

$^a$ n(S)→Ph (also); $^b$ CBZ→Ph (mainly).

**Figure S18.** Crystal molecular dimers with the shortest intermolecular distance. Eclipsed (left) and T-shape (right) molecular pairs of CBZ-SO in the crystal. CBZ-SO and CBZ-SO$_2$ crystals exhibit equivalent molecular pairs.
Table S7. Vertical excitation energies (in eV), oscillator strengths ($f$ in parenthesis) to the lowest singlet and triplet states of computed for the eclipsed and T-shape molecular pairs of CBZ-SO$_n$ in the crystal (Figure S17) computed at the oB97X-D/6-31+G(d) level.

| state  | CBZ-S  | CBZ-SO | CBZ-SO$_2$ |
|--------|--------|--------|------------|
|        | CBZ-S  | CBZ-SO | CBZ-SO$_2$ |
|        | CBZ-S  | CBZ-SO | CBZ-SO$_2$ |
|        | CBZ-S  | CBZ-SO | CBZ-SO$_2$ |
|        | CBZ-S  | CBZ-SO | CBZ-SO$_2$ |
| eclipsed pair | | | |
| T$_1$  | 3.24   | 3.23   | 3.29       |
| T$_2$  | 3.24   | 3.24   | 3.29       |
| T$_3$  | 3.24   | 3.24   | 3.29       |
| T$_4$  | 3.28   | 3.25   | 3.30       |
| S$_1$  | 4.32 (0.166) | 4.34 (0.022) | 4.41 (0.009) |
| S$_2$  | 4.33 (0.150) | 4.37 (0.451) | 4.43 (0.062) |
| S$_3$  | 4.34 (0.135) | 4.37 (0.144) | 4.44 (0.503) |
| S$_4$  | 4.35 (0.010) | 4.40 (0.134) | 4.48 (0.143) |
| T-shape pair | | | |
| T$_1$  | 3.22   | 3.22   | 3.28       |
| T$_2$  | 3.23   | 3.23   | 3.30       |
| T$_3$  | 3.24   | 3.23   | 3.30       |
| T$_4$  | 3.25   | 3.25   | 3.31       |
| S$_1$  | 4.32 (0.664) | 4.34 (1.144) | 4.41 (1.117) |
| S$_2$  | 4.35 (0.118) | 4.36 (0.005) | 4.45 (0.001) |
| S$_3$  | 4.36 (0.093) | 4.41 (0.017) | 4.48 (0.117) |
| S$_4$  | 4.38 (0.100) | 4.42 (0.171) | 4.49 (0.177) |
Table S8. Relative energies (in meV) and SOCs (in cm$^{-1}$) between the lowest excited singlet ($S_1$) and energetically close triplets of the CBZ-SO$_n$ dimers computed at the oB97X-D/6-31+G(d) level in the crystal molecular structure. The last column qualitatively indicates the weight of the sulfur and oxygen lone pairs participation in the electronic structure of $T_n$.

| molecule | state | $E(S_1)$-$E(T_n)$ | SOC | n(S) or n(O) character |
|----------|-------|--------------------|-----|------------------------|
| CBZ-S    | $T_7$ | 211                | 0.8 | large                  |
|          | $T_8$ | 163                | 0.6 | small                  |
|          | $T_9$ | 162                | 0.2 | small                  |
|          | $T_{10}$ | 82               | 0.8 | small                  |
|          | $T_{11}$ | 79               | 0.3 | small                  |
|          | $T_{12}$ | 34               | 0.4 | large                  |
|          | $T_{13}$ | -281             | 0.0 | small                  |
|          | $T_{14}$ | -313             | 0.8 | small                  |
|          | $T_{15}$ | -376             | 0.2 | small                  |
|          | $T_{16}$ | -377             | 0.5 | small                  |
|          | $T_{17}$ | -432             | 0.7 | small                  |
|          | $T_{18}$ | -433             | 0.5 | small                  |
|          | $T_{19}$ | -605             | 3.1 | large                  |
|          | $T_{20}$ | -642             | 0.2 | small                  |
| CBZ-SO   | $T_7$ | 360                | 8.6 | large                  |
|          | $T_8$ | 182                | 3.6 | small n(s), n(O)       |
|          | $T_9$ | 175                | 0.8 | no                     |
|          | $T_{10}$ | 93               | 0.9 | no                     |
|          | $T_{11}$ | 85               | 0.4 | no                     |
|          | $T_{12}$ | -3               | 3.3 | small n(O)             |
|          | $T_{13}$ | -70              | 2.7 | small n(S), n(O)       |
|          | $T_{14}$ | -196             | 5.6 | small n(S), n(O)       |
|          | $T_{15}$ | -253             | 2.5 | small n(S), n(O)       |
|          | $T_{16}$ | -328             | 3.2 | small n(S), n(O)       |
|          | $T_{17}$ | -334             | 1.5 | small n(S)             |
|          | $T_{18}$ | -369             | 4.1 | small n(O)             |
|          | $T_{19}$ | -394             | 0.4 | no                     |
|          | $T_{20}$ | -472             | 36.9| large n(O), n(S)       |
| CBZ-SO$_2$| $T_7$ | 197                | 0.2 | no                     |
|          | $T_8$ | 197                | 0.5 | no                     |
|          | $T_9$ | 121                | 1.0 | no                     |
|          | $T_{10}$ | 120              | 0.1 | no                     |
|          | $T_{11}$ | -31              | 0.3 | no                     |
|          | $T_{12}$ | -47              | 0.3 | no                     |
|          | $T_{13}$ | -204             | 0.4 | no                     |
|          | $T_{14}$ | -213             | 0.3 | no                     |
|          | $T_{15}$ | -297             | 0.4 | no                     |
|          | $T_{16}$ | -297             | 0.3 | no                     |
|          | $T_{17}$ | -339             | 0.4 | no                     |
|          | $T_{18}$ | -339             | 0.1 | no                     |
|          | $T_{19}$ | -477             | 0.3 | small n(O)             |
|          | $T_{20}$ | -490             | 0.4 | small n(O)             |
Figure S19. Spin orbit couplings (in cm$^{-1}$) between excited triplet states and $S_1$ (red), $S_2$ (blue) and $S_3$ (green) of CBZ-SO$_n$ for the crystal molecular structure calculated at the oB97X-D/6-31+G(d) level. Dashed vertical lines indicate the energy of the excited singlet, $S_1$, $S_2$ or $S_3$, respectively.

Figure S20. Molecular orbital sulfur lone pair of CBZ-S (left) and CBZ-SO (right) responsible for the strong $S_1/T_n$ SOC in the crystal molecular structure calculated at the oB97X-D/6-31+G(d) level.
Phosphorescent emission probability

We evaluate the oscillator strength of triplet emission through perturbation theory by expanding the triplet state wave function as:

\[ |T_1^{SOC}\rangle = |T_1\rangle + \sum_n \frac{\langle S_n | \hat{H}_{SO} | T_1 \rangle}{E(T_1) - E(S_n)} |S_n\rangle \]  (S1)

Then, the oscillator strength \( f \) can be expressed as:

\[ f = \frac{2}{3} \Delta E_{ST} |\langle T_1^{SOC} | \hat{\mu} | S_0 \rangle|^2 \]  (S2)

Table S9. Oscillator strengths \( f \) for the emission from the two lowest excited triplet states of \( \text{CBZ-SO}_n \) computed with equation S2 and with the sum over excited singlets in equation S1 running over the 20 lowest states. Computations have been done for the molecular crystal structures at the oB97X-D/6-31+G(d) level.

| state | CBZ-S | CBZ-SO | CBZ-SO₂ |
|-------|-------|--------|---------|
| \( T_1 \) | 4.7·10⁻⁹ | 6.2·10⁻⁹ | 2.5·10⁻⁸ |
| \( T_2 \) | 2.6·10⁻⁹ | 8.1·10⁻⁹ | 1.1·10⁻⁸ |
## Optimized geometries

**CBZ-S: $S_0$ state**

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| S    | 24.92617 | 1.689602 | 4.065272 |
| C    | 24.794085 | 2.814206 | 2.686971 |
| C    | 23.90706 | 3.895676 | 2.703404 |
| H    | 23.311695 | 4.095619 | 3.588990 |
| C    | 23.806723 | 4.732051 | 1.599733 |
| C    | 24.556661 | 4.470791 | 0.450104 |
| C    | 25.423712 | 3.80125 | 0.422228 |
| C    | 25.557303 | 2.567225 | 1.544729 |
| H    | 26.253992 | 1.734225 | 1.529416 |
| C    | 25.065154 | 2.814206 | 5.443572 |
| H    | 23.141118 | 5.899373 | 1.619348 |
| N    | 24.436517 | 3.13492 | -0.679729 |
| C    | 25.998464 | 3.175939 | -0.476225 |
| C    | 24.301941 | 2.567225 | 6.585818 |
| C    | 25.951531 | 3.895677 | 5.427136 |
| C    | 23.258015 | 5.581133 | -1.371620 |
| C    | 25.473592 | 6.020986 | -1.282257 |
| H    | 26.052538 | 1.734223 | 6.601133 |
| C    | 24.435536 | 3.380124 | 7.708319 |
| H    | 26.547539 | 4.095621 | 4.541547 |
| C    | 26.052518 | 4.732052 | 6.530806 |
| C    | 21.974142 | 5.079241 | -1.153623 |
| C    | 23.538372 | 6.469123 | -2.430806 |
| C    | 24.958303 | 6.751507 | -2.373217 |
| C    | 26.820668 | 6.088544 | -0.923667 |
| H    | 23.860788 | 3.175938 | 8.606773 |
| C    | 25.302585 | 4.470791 | 7.680438 |
| H    | 26.718122 | 5.589939 | 6.511189 |
| C    | 20.965764 | 5.500074 | -2.012170 |
| H    | 21.769294 | 4.380541 | -0.348272 |
| C    | 22.508111 | 6.877282 | -3.280466 |
| C    | 25.812769 | 7.554248 | -3.131686 |
| H    | 27.207238 | 5.537422 | -0.071898 |
| C    | 27.651057 | 6.894227 | -1.693373 |
| N    | 25.422733 | 5.313493 | 8.810271 |
| C    | 21.224389 | 6.392938 | -3.064263 |
| H    | 19.956537 | 5.125819 | -1.865850 |
| H    | 22.709668 | 7.561218 | -4.100480 |
| H    | 25.429387 | 8.122307 | -3.974984 |
| C    | 27.157466 | 7.619020 | -2.789663 |
| H    | 28.704406 | 6.965093 | -1.437512 |
| C    | 24.385659 | 6.020985 | 9.412804 |
| C    | 26.601238 | 5.581136 | 9.502157 |
| H    | 20.412798 | 6.702129 | -3.716025 |
| H    | 27.834077 | 8.238425 | -3.370686 |
| C    | 23.038582 | 6.088540 | 9.054220 |
| C    | 24.900952 | 6.751507 | 10.503761 |
| C    | 27.885111 | 5.079246 | 9.284153 |
| C    | 26.320884 | 6.469125 | 10.561343 |
| H    | 22.652009 | 5.537417 | 8.202453 |
| C    | 22.208195 | 6.894221 | 9.823930 |
| C    | 24.046488 | 7.554246 | 11.262235 |
| H    | 28.089956 | 4.380546 | 8.478802 |
| C    | 28.893492 | 5.500080 | 10.142696 |
| C    | 27.351149 | 6.877286 | 11.410999 |
| H    | 21.154845 | 6.965086 | 9.568074 |
CBZ-SO: $S_0$ state

| Element | X  | Y  | Z  |
|---------|----|----|----|
| S       | 26.082388 | 1.181616 | 3.991448 |
| C       | 25.720475 | 2.382716 | 2.683268 |
| C       | 24.402824 | 2.742458 | 2.420725 |
| H       | 23.583931 | 2.297981 | 2.981302 |
| C       | 24.136994 | 3.691988 | 1.439182 |
| H       | 23.118258 | 4.008510 | 1.237036 |
| C       | 25.188142 | 4.245220 | 0.705576 |
| C       | 25.004475 | 3.845127 | 0.951801 |
| C       | 26.773828 | 2.915738 | 1.948950 |
| H       | 27.788015 | 2.581566 | 2.150361 |
| O       | 27.455873 | 0.632756 | 3.713001 |
| C       | 26.287885 | 2.406876 | 5.315942 |
| N       | 24.920461 | 5.209314 | -0.291868 |
| H       | 27.304336 | 4.262281 | 0.352934 |
| C       | 25.174737 | 2.998337 | 5.906214 |
| C       | 27.575482 | 2.715839 | 5.734017 |
| C       | 24.067884 | 5.043049 | -1.381667 |
| C       | 25.450161 | 6.497959 | -0.336212 |
| H       | 24.169114 | 2.730888 | 5.591024 |
| C       | 25.356152 | 3.934399 | 6.916999 |
| H       | 28.420424 | 2.218601 | 5.265643 |
| C       | 27.755409 | 3.665778 | 6.734957 |
| C       | 23.340464 | 3.917203 | -1.769822 |
| C       | 24.050709 | 6.234300 | -2.135942 |
| C       | 24.934953 | 7.163388 | -1.465741 |
| C       | 26.318930 | 7.126610 | 0.556798 |
| H       | 24.502364 | 4.397091 | 7.402540 |
| C       | 26.648126 | 4.277155 | 7.324846 |
| H       | 28.754042 | 3.943806 | 7.058337 |
| C       | 22.574908 | 4.014113 | -2.925652 |
| H       | 23.375733 | 2.994587 | -1.198693 |
| C       | 23.274153 | 6.307147 | -3.294039 |
| C       | 25.312230 | 8.486808 | -1.718322 |
| H       | 26.697152 | 6.614595 | 1.436235 |
| C       | 26.679622 | 8.440833 | 0.284419 |
| N       | 26.830177 | 5.242815 | 8.340375 |
| C       | 22.535485 | 5.196377 | -3.681194 |
| H       | 21.998528 | 3.152940 | -3.251417 |
| H       | 23.252017 | 7.218785 | -3.884962 |
| H       | 24.923442 | 9.013667 | -2.585520 |
| C       | 26.187169 | 9.116995 | -0.842761 |
| H       | 27.355907 | 8.954230 | 0.961905 |
| C       | 26.355912 | 6.552881 | 8.308372 |
| C       | 27.520524 | 5.050697 | 9.535802 |
| H       | 21.926331 | 5.238142 | -4.579072 |
| H       | 26.490846 | 10.143103 | -1.026855 |
| C       | 25.642886 | 7.209685 | 7.304392 |
| C       | 26.743377 | 7.209738 | 9.494432 |
| C       | 28.140916 | 3.899143 | 10.022108 |
CBZ-SO₂: S₀ state

C 17.899985 12.089477 -0.413436
C 17.771094 11.098540 0.011200
C 19.978695 12.205189 0.146628
C 16.830384 12.720056 -1.036022
C 19.151543 12.719244 -0.334412
C 15.864332 12.227881 -1.107714
C 17.015498 13.994836 -1.574271
C 19.359853 13.987857 -0.862671
C 16.150748 14.909593 -2.292222
C 18.274963 14.619576 -1.471860
C 20.335364 14.460802 -0.807219
C 14.810070 14.860785 -2.678868
C 16.923861 16.048191 -2.59503
C 18.213412 15.866741 -2.094706
C 14.203160 13.988921 -2.450518
C 14.263713 15.944771 -3.353778
C 16.379920 17.149009 -3.259446
C 19.280367 16.782027 -2.208754
C 13.228445 15.921338 -3.661893
C 15.043592 17.077231 -3.634570
C 16.970097 18.035730 -3.468619
C 19.658511 17.258785 -3.466673
C 19.954568 17.211681 -1.062215
C 14.594770 17.919828 -4.152560
C 20.709739 18.160302 -3.501814
C 19.131646 16.913531 -4.350697
C 19.631202 16.858550 -0.088071
C 21.017328 18.099179 -1.173357
C 21.004694 18.549708 -4.549412
C 21.385287 18.565206 -2.432646
C 21.538203 18.453311 -0.289368
C 22.778332 19.675083 -2.582790
O 22.639736 20.386257 -3.851304
O 24.171376 18.565206 -2.732034
O 22.916927 20.386257 -1.314277
C 24.539335 18.099180 -3.992224
C 24.846924 18.160302 -1.585397
C 24.018460 18.453311 -4.876213
C 25.602095 17.211681 -4.103366
H 24.551969 18.549708 -0.616169
C 25.898152 17.258785 -1.698908
|     |       |              |            |            |
|-----|-------|--------------|------------|------------|
|     |       | 25.925461    | 16.858550 | -5.077509 |
|     |       | 26.276296    | 16.782027 | -2.956826 |
|     |       | 26.425016    | 16.913530 | -0.814884 |
|     |       | 27.343251    | 15.866741 | -3.070875 |
|     |       | 27.281701    | 16.619576 | -3.693721 |
|     |       | 28.632803    | 16.048191 | -2.569078 |
|     |       | 28.541165    | 13.987857 | -4.302910 |
|     |       | 29.405915    | 14.909593 | -2.873358 |
|     |       | 29.176743    | 17.149009 | -1.906134 |
|     |       | 29.405120    | 14.719244 | -4.831169 |
|     |       | 25.221299    | 14.460802 | -4.358362 |
|     |       | 28.726279    | 12.720056 | -4.125959 |
|     |       | 30.746593    | 14.860785 | -2.486713 |
|     |       | 28.586566    | 18.035730 | -1.696962 |
|     |       | 30.513071    | 17.077231 | -1.531011 |
|     |       | 25.577968    | 12.205189 | -5.312209 |
|     |       | 27.656678    | 12.089478 | -4.752145 |
|     |       | 29.692331    | 12.227881 | -4.057867 |
|     |       | 31.355030    | 13.988921 | -2.715063 |
|     |       | 31.292950    | 15.924771 | -1.811802 |
|     |       | 30.961893    | 17.919828 | -1.013020 |
|     |       | 27.785569    | 11.098540 | -5.176781 |
|     |       | 32.333819    | 15.921338 | -1.506781 |

References
1. Cheng, Z.; Sun, P.; Tang, A.; Jin, W.; Liu, C. Org. Lett. 2019, 21, 8925–8929.
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.; J. Appl. Cryst. 2009, 42, 339–341.
3. Sheldrick, G. M. Acta Cryst. 2015, A71, 3–8.
4. L. Xu, K. Zhou, H. Ma, A. Lv, D. Pei, G. Li, Y. Zhang, Z. An, A. Li and G. He, ACS Appl Mater Interfaces, 2020, 12, 18385–18394.
5. S. Xu, T. Liu, Y. Mu, Y.-F. Wang, Z. Chi, C.-C. Lo, S. Liu, Y. Zhang, A. Lien and J. Xu, Angew. Chem. Int. Ed., 2014, 54, 874–878.
6. Chai, J.-D.; Head-Gordon, M. Phys Chem Chem Phys 2008, 10, 6615–6620.
7. Liu, F.; Livshits, E.; Lochan, R. C.; Luenser, A.; Manohar, P.; Manzer, S. F.; Mao, S.-P.; Mardirossian, N.; Marenich, A. V.; Maurer, S. A.; Mayhall, N. J.; Neuscamman, E.; Oana, C. M.; Olivares-Amaya, R.; O’Neill, D. P.; Parkhill, J. A.; Perrine, T. M.; Peberati, R.; Prociuk, A.; Rehn, D. R.; Rosta, E.; Russ, N. J.; Sharada, S. M.; Sharma, S.; Small, D. W.; Sodt, A.; Stein, T.; Stueck, D.; Su, Y.-C.; Thom, A. J. W.; Tsuchimochi, T.; Vanovschi, V.; Vogt, L.; Vydrov, O.; Wang, T.; Watson, M. A.; Wenzel, J.; White, A.; Williams, C. F.; Yang, J.; Yeganeh, S.; Yost, S. R.; You, Z.-Q.; Zhang, I. Y.; Zhang, X.; Zhao, Y.; Brooks, B. R.; Chan, G. K. L.; Chipman, D. M.; Cramer, C. J.; Goddard, W. A.;
Gordon, M. S.; Hehre, W. J.; Klamt, A.; Schaefer, H. F.; Schmidt, M. W.; Sherrill, C. D.; Truhlar, D. G.; Warshel, A.; Xu, X.; Aspuru-Guzik, A.; Baer, R.; Bell, A. T.; Besley, N. A.; Chai, J.-D.; Dreuw, A.; Dunietz, B. D.; Furlani, T. R.; Gwaltney, S. R.; Hsu, C.-P.; Jung, Y.; Kong, J.; Lambrecht, D. S.; Liang, W.; Ochsenfeld, C.; Rassolov, V. A.; Slipchenko, L. V.; Subotnik, J. E.; Van Voorhis, T.; Herbert, J. M.; Krylov, A. I.; Gill, P. M. W.; Head-Gordon, M.; Shao, Y.; Gan, Z.; Epifanovsky, E.; Gilbert, A. T. B.; Wormit, M.; Kussmann, J.; Lange, A. W.; Behn, A.; Deng, J.; Feng, X.; Ghosh, D.; Goldey, M.; Horn, P. R.; Jacobson, L. D.; Kaliman, I.; Khaliullin, R. Z.; Kus, T.; Landau, A.; Liu, J.; Proynov, E. I.; Rhee, Y. M.; Richard, R. M.; Rohrdanz, M. A.; Steele, R. P.; Sundstrom, E. J.; Woodcock, H. L.; Zimmerman, P. M.; Zuev, D.; Ben Albrecht; Alguire, E.; Austin, B.; Beran, G. J. O.; Bernard, Y. A.; Berquist, E.; Brandhorst, K.; Bravaya, K. B.; Brown, S. T.; Casanova, D.; Chang, C.-M.; Chen, Y.; Chien, S. H.; Closser, K. D.; Crittenden, D. L.; Diedenhofen, M.; Distasio, R. A.; Do, H.; Dutoi, A. D.; Edgar, R. G.; Fathehi, S.; Fusti-Molnar, L.; Ghysels, A.; Golubeva-Zadorozhnaya, A.; Gomes, J.; Hanson-Heine, M. W. D.; Harbach, P. H. P.; Hauser, A. W.; Hohenstein, E. G.; Holden, Z. C.; Jagau, T.-C.; Ji, H.; Kaduk, B.; Khistyaev, K.; Kim, J.; Kim, J.; King, R. A.; Klunzinger, P.; Kosenkov, D.; Kowalczyk, T.; Krauter, C. M.; Lao, K. U.; Laurent, A. D.; Lawler, K. V.; Levchenko, S. V.; Lin, C. Y. Molecular Physics 2015, 113, 184–215.