Enhanced Photoluminescence of Sulfur-Bridged Organic Chromophores

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Experimental Details

General

Electronic absorption spectroscopy was performed on a Varian Cary 5000 spectrophotometer. Corrected emission measurements were performed on a PTI QuantaMaster 50 fluorimeter at room temperature in CH₂Cl₂ (unless otherwise specified). All solvents used for photochemical measurements, dichloromethane, cyclohexane, and acetonitrile were analytical HPLC grade, and used as received from Fisher Scientific. Samples were purged with argon for no less than 15 min before emission studies. Photoluminescence quantum yields (Φ_f) for each compound were calculated according to equation S1, using 9-cyanoanthracene as a standard.

$$\Phi_x = \left(\frac{A_s}{A_x} \right) \left(\frac{F_x}{F_s} \right) \left(\frac{n_x}{n_s} \right)^2 \Phi_s \quad \text{equation S1.}$$

A is the absorption at the excitation wavelength for the standard (s) and the compound of interest (x), F is the integrated area under the emission spectrum, n is the refractive index of the solvent and Φ_s is the known quantum yield for the standard in a given solvent ($\Phi_{9\text{-cyanoanthracene}} = 0.80$ in methanol, excited at 364 nm).¹ The following excitation wavelengths were used for the compounds: for all **1SO_n** = 335 nm, **2SO_n** = 375 nm, **3SO_n** = 304 nm, and **4SO_n** = 362 nm. To correct for excitation intensity variation as a function of wavelength, the relative intensity of the excitation light at each wavelength was determined by integrating the excitation profile obtained with no sample present. The collected emission spectra (F) for the samples were then scaled relative to the excitation intensity at 364 nm where the standard was excited.

To analyze the statistical significance of this method, and to ascertain the statistical significance of the observed increase in Φ_f as a function of the bridging sulfur oxidation state, data was collected for each sample at three different concentrations for all compounds including 9-cyanoanthracene. The Φ_f was calculated using equation S1 at each concentration and the resulting data was plotted against the known concentrations. The standard deviation in Φ_f was calculated using the measured Φ_f at different concentrations.

Nuclear magnetic resonance (NMR) experiments were performed on either a 300, 400, or 600 MHz Bruker spectrometer in deuterated chloroform (CDCl₃) or dichloromethane (CD₂Cl₂). Compounds **1** and **2** were characterized by 1-dimensional ¹H NMR only. The structures of compounds **3** and **4** were assigned using 2-dimensional NMR experiments, including COSY, ¹H-¹³C HSQC, and HMBC.

Infrared spectroscopy (IR) was performed on an attenuated total reflection (ATR) crystal using a Perkin-Elmer Frontier FT-IR spectrometer.

Solid-state photoluminescence measurements were made on pre-cleaned quartz slides (sonicated 15 min each in methanol, chloroform, and again with methanol and allowed to dry in an oven for several hours), and ~1 cm² alumina TLC plates without added fluorescent indicator.

Equations S1-S3 were generated using open source web-based software, <http://www.codecogs.com/latex/eqneditor.php>.

Synthetic Details

Synthesis of **1S**

To a solution of 2,2'-bithiophene (363 mg, 2.18 mmol) in dry tetrahydrofuran (8.0 mL) at -78 °C under nitrogen was slowly added *n*-butyllithium (1.6 M in hexanes, 1.40 mL, 2.24 mmol). The mixture was stirred for 1 h. To the resultant mixture was added drop-wise a solution of bis(phenylsulfonyl)sulfide (366 mg, 1.16 mmol) in dry tetrahydrofuran (5.0 mL) and the mixture was stirred overnight. The mixture was poured over water (25 mL) and extracted with diethylether (3 × 15 mL). The organic layers were combined and dried over anhydrous magnesium sulfate, filtered, and concentrated under vacuum. Purification by column chromatography (hexanes) gave a yellow-white solid. Yield: 255 mg, 65%. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.26 (dd, 2H, *J* = 1.3, 5.1 Hz), 7.17-7.15 (m, 4H), 7.05 (d, 2H, *J* = 3.7 Hz), 7.01 (dd, 2H, *J* = 3.7, 5.0 Hz). HRMS (ESI): *m/z* calculated: 361.9386, found 361.9389.

Synthesis of **1SO**

To a solution of **1** (129 mg, 0.356 mmol) in dichloromethane (6.0 mL) at 0 °C was added *meta*-chloroperoxybenzoic acid (70%, 89 mg, 0.36 mmol) and the mixture was stirred for 15 min. The reaction mixture was poured over a saturated aqueous solution of sodium bicarbonate (15 mL) and ice, and was then extracted with dichloromethane (3 × 10 mL). The organic layers were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated under vacuum. Purification by column chromatography (dichloromethane) gave a white solid. Yield: 86 mg, 64%. ¹H NMR (300 MHz, CDCl₃): δ 7.47 (d, 2H, *J* = 3.9 Hz), 7.31 (dd, 2H, *J* = 1.3, 5.1 Hz), 7.24, (dd, 2H, *J* = 1.4, 3.7 Hz), 7.15 (d, 2H, *J* = 3.9 Hz), 7.04 (dd, 2H, *J* = 3.7, 5.0 Hz). HRMS (ESI): *m/z* calculated: 378.9413, found 378.9416. IR (neat): (σ SO) 1049 cm⁻¹.

Synthesis of **1SO₂**

To a solution of **1** (202 mg, 0.558 mmol) in dichloromethane (9.3 mL) at 0 °C was added *meta*-chloroperoxybenzoic acid (70%, 274 mg, 1.11 mmol) and the mixture was stirred for 15 min. The reaction mixture was poured over a saturated aqueous solution of sodium bicarbonate (20 mL) and ice and extracted with dichloromethane (3 × 15 mL). The organic layers were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The crude material was purified

by column chromatography (2:1 hexanes: dichloromethane) to afford a white solid. Yield: 122 mg, 55%. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.64 (d, 2H, $J = 3.9$ Hz), 7.34 (dd, 2H, $J = 1.2, 5.1$ Hz), 7.27-7.26 (m, 2H), 7.12 (d, 2H, $J = 4.1$ Hz), 7.06 (dd, $J = 3.7, 5.0$ Hz). HRMS (ESI): m/z calculated: 393.9284, found 393.9285. IR (neat): (σ SO_2) 1147 cm^{-1} , and 1328 cm^{-1} .

Synthesis of 2S

Prepared in the same manner as 1S.

Yield yellow solid: 53%. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.26 (dd, 2H, $J = 0.9$ Hz, 5.2 Hz), 7.20 (dd, 2H, $J = 0.9$ Hz, 3.5 Hz), 7.16 (d, 2H, $J = 3.6$ Hz), 7.09 (d, 2H, $J = 3.6$ Hz), 7.07 (d, 2H, $J = 3.9$ Hz), 7.05 (d, 2H, $J = 3.6$ Hz), 7.04 (d, 2H, $J = 3.6$ Hz), 7.03 (d, 2H, $J = 3.6$ Hz). HRMS (ESI): m/z calculated: 525.9141, found 525.9144.

Synthesis of 2SO

Prepared in the same manner as 1SO.

Yield yellow solid: 79%. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.50 (d, 2H, $J = 4.0$ Hz), 7.33 (dd, 2H, $J = 1.2, 5.2$ Hz), 7.27, (dd, 2H, $J = 0.9, 3.5$ Hz), 7.22 (d, 2H, $J = 3.9$ Hz), 7.21 (d, 2H, $J = 3.9$ Hz), 7.17 (d, 2H, $J = 3.6$ Hz), 7.09 (d, 1H, $J = 3.7$ Hz), 7.08 (d, 1H, $J = 3.7$ Hz). HRMS (ESI): m/z calculated: 542.9168, found 542.9167. IR (neat): (σ SO) 1047 cm^{-1} .

Synthesis of 2SO₂

Prepared in the same manner as 1SO₂.

Yield yellow solid: 45%. ^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, 2H, $J = 3.9$ Hz), 7.31 (dd, 2H, $J = 0.9, 5.1$ Hz), 7.25, (d, 2H, $J = 1.4, 3.4$ Hz), 7.23 (d, 2H, $J = 3.6$ Hz), 7.15 (dd, 2H, $J = 1.2, 4.0$ Hz), 7.07 (d, 1H, $J = 3.7$ Hz), 7.06 (d, 1H, $J = 3.6$ Hz). HRMS (ESI): m/z calculated: 557.9039, found 557.9047. IR (neat): (σ SO) 1019, 1148 cm^{-1} , and 1330 cm^{-1} .

Synthesis of 3S

Prepared in the same manner as 1S.

Recrystallized from DCM. Yield colorless crystals: 30%. ^1H NMR (600 MHz, CD_2Cl_2): δ 8.45 (m, 2H, **H₉**), 7.95 (m, 2H, **H₆**), 7.85 (m, 2H, **H₄**), 7.58 (m, 4H, **H₇/H₈**), 7.37 (m, 4H, **H₇/H₈**). ^{13}C NMR (600 MHz, CD_2Cl_2): δ 133.69 (**C₅**), 132.05 (**C₁₀**), 131.85 (**C₁**), 129.52 (**C₂**), 128.13 (**C₆**), 127.56 (**C₄**), 126.28 (**C₈**), 125.97 (**C₇**), 125.37 (**C₃**), 124.40 (**C₉**). ^1H NMR (ESI): m/z calculated: 286.0816, found 286.0820.

Synthesis of 3SO

Prepared in the same manner as 1SO.

Yield white solid: 56%. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.35 (m, 2H), 8.04 (dd, 2H, $J = 0.91, 7.31$ Hz), 7.99, (d, 2H, $J = 7.31$ Hz), 7.61 (d, 1H), 7.58 (d, 1H, $J = 8.22$ Hz), 7.55 (m, 4H). HRMS (ESI): calculated m/z 303.0844, found 303.0846. IR (neat): (σ SO) 1041 cm^{-1} .

Synthesis of 3SO₂

Prepared in the same manner as ISO₂.

Yield white solid: 17%. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.64 (dd, 2H), 8.56 (m, 2H), 8.15, (dd, 2H, *J* = 8.6 Hz), 7.94 (m, 2H, *J* = 2.7, 6.7 Hz), 7.72 (d, 2H, *J* = 7.6 Hz), 7.70 (d, 2H, *J* = 8.3 Hz), 7.55 (m, 2H). HRMS (EI): calculated *m/z* 318.07145, found 318.07117. IR (neat): (σ SO) 1119, 1155 cm⁻¹ and 1306 cm⁻¹.

Synthesis of 4S

Prepared in the same manner as IS.

Yield yellow solid 86%. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.77 (d, 2H, *J* = 9.14 Hz, **H₁₃**), 8.25 (d, 4H, *J* = 7.61 Hz, **H₁₀**), 8.17, (d, 2H, *J* = 9.14 Hz, **H₈**), 8.12 (d, 1H, *J* = 8.83 Hz, **H₁₂**), 7.08 (d, 1H, *J* = 7.31 Hz, **H₆**), 8.05 (d, 2H, *J* = 7.31 Hz, **H₉**), 8.04 (d, 2H, *J* = 8.83 Hz, **H₅**), 8.03 (d, 2H, *J* = 8.22 Hz, **H₃**), 7.85 (d, 2H, *J* = 8.22 Hz, **H₂**). ¹³CNMR (600 MHz, CD₂Cl₂): δ 131.91 (**C₇**), 131.57 (**C₁₁**), 131.38 (**C₄**), 131.30 (**C₁₄**), 130.90 (**C₁**), 130.58 (**C₂**), 128.92 (**C₁₂**), 128.25 (**C₆**), 127.79 (**C₅**), 126.95 (**C₉**), 126.13 (**C₈**), 126.08 (**C₁₀**), 125.89 (**C₁₅**), 125.80 (**C₃**), 124.97 (**C₁₆**), 124.75 (**C₁₂**). HRMS (ESI): calculated *m/z* 434.1129, found 434.1128.

Synthesis of 4SO

Prepared in the same manner as ISO.

Yield yellow solid: 30%. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.75 (d, 2H, *J* = 9.22 Hz, **H₁₃**), 8.56 (d, 2H, *J* = 8.19 Hz, **H₂**), 8.29, (d, 2H, *J* = 8.19 Hz, **H₃**), 8.27 (d, 2H, *J* = 8.88 Hz, **H₈**), 8.25 (d, 2H, *J* = 8.19 Hz, **H₁₀**), 8.20 (d, 2H, *J* = 9.56 Hz, **H₁₂**), 8.17 (d, 2H, *J* = 9.22 Hz, **H₆**), 8.09 (d, 2H, *J* = 8.88 Hz, **H₅**), 8.07 (1H, *J* = 7.51, **H₉**), 8.05 (1H, *J* = 7.85, **H₉**). ¹³CNMR (400 MHz, CD₂Cl₂): δ 137.76 (**C₁**), 133.43 (**C₄**), 131.23 (**C₇**), 130.52 (**C₁₁**), 129.64 (**C₁₂**), 129.41 (**C₆**), 128.67 (**C₁₄**), 127.28 (**C₅**), 126.77 (**C₉**), 126.49 (**C₁₀**), 125.60 (**C₃**), 124.65 (**C₁₅**), 124.34 (**C₁₆**), 123.46 (**C₂**), 121.50 (**C₁₃**). HRMS (EI): calculated *m/z* 450.10784, found 450.10760. IR (neat): (σ SO) 1046 cm⁻¹

Synthesis of 4SO₂

Prepared in the same manner as ISO₂.

Yield yellow solid: 24%. ¹H NMR (400 MHz, CD₂Cl₂): δ 9.16 (d, 2H, *J* = 8.22 Hz), 8.95 (d, 2H, *J* = 9.44 Hz), 8.43, (d, 2H, *J* = 8.53 Hz), 8.30 (d, 2H, *J* = 7.61 Hz), 8.25 (d, 4H, *J* = 8.83 Hz), 8.17 (dd, 4H, *J* = 2.13, 9.14 Hz), 8.08 (d, 1H, *J* = 7.61 Hz), 8.06 (d, 1H, *J* = 7.61 Hz). HRMS (ESI): *m/z* calculated: 467.1106, found 467.1104. IR (neat): (σ SO) 1122, 1153 cm⁻¹, and 1296 cm⁻¹.

DFT Calculations

All calculations were performed with the 2012.01 version of the Amsterdam Density Functional (ADF) program.² All electrons were included in the variational treatment (i.e., no frozen-core approximation was applied). C_1 (NOSYM) symmetry-unrestricted and C_2 and C_s symmetry-restricted geometry optimizations for **1SO_n** and **2SO_n** yielded similar results for orbital energies and compositions in each case for different conformations of the thiophene rings relative to the central S atom. Energies, geometries, bond orders,³ atomic charges,⁴ and the orbital electronic structure were calculated using the generalized gradient approximation (GGA) of density functional theory (DFT) at the BP86 level. The GGA proceeds from the local density approximation (LDA), where exchange is described by Slater's $X\alpha$ potential^{2h} and correlation is treated in the Vosko-Wilk-Nusair (VWN) parameterization,²ⁱ and is augmented with nonlocal corrections to exchange due to Becke^{2j,k} and correlation due to Perdew^{2l} added self-consistently.^{2m} Relativistic effects were taken into account in all cases using the zeroth-order relativistic approximation (ZORA)⁵ and all-electron TZ2P basis sets from the ADF ZORA basis sets library were used for all atoms.^{2f} TDDFT excited state geometries for **2S**, **2SO**, and **2SO2** were calculated for the lowest singlet excited state of each. All other parameters were the same as for the BP86 ground state geometry optimizations.

DFT Data

Figure S1. Calculated frontier molecular orbitals for 1SO_n.

Figure S2. Calculated frontier molecular orbitals for 2SO_n .

Table S1. Ground-state (GS) and excited-state (ES) atomic charges for **2SO_n**.

Compound	q Bader	q Hirshfeld	q Voronoi
2S GS	0.174	0.024	-0.001
2S ES	0.189	0.053	0.009
2S Δ(ES - GS)	0.015	0.029	0.010
2SO GS	1.351	0.287	0.314
2SO ES	1.328	0.271	0.299
2SO Δ(ES - GS)	-0.023	-0.016	-0.015
2SO ₂ GS	2.550	0.399	0.451
2SO ₂ ES	2.531	0.384	0.441
2SO ₂ Δ(ES -GS)	-0.019	-0.015	-0.010

Table S2. Ground-state (GS) and excited-state (ES) bond lengths, and angles for **2SO_n**.

Compound	C-S-C Angle	C-S-O Angle	O-S-O Angle	C-S Distance (pm)	S-O Distance (pm)	C-C bridge center	C-C bridge outer
2S GS	105.0			175.8		144.0	144.1
2S ES	105.8			175.0		141.3	142.0
2S Δ(ES - GS)	0.8			-0.8		-2.7	-1.9
2SO GS	101.4	105.2		180.3	176.3	144.3	144.3
2SO ES	101.3	105.7		179.6	175.5	141.5	141.8
2SO Δ(ES - GS)	0.0	0.5		-0.7	-0.8	-2.8	-2.5
2SO ₂ GS	108.0	106.3	123.2	176.3	145.5	144.3	144.2
2SO ₂ ES	109.8	106.0	123.5	175.5	145.7	142.1	141.8
2SO ₂ Δ(ES -GS)	1.8	-0.3	0.2	-0.8	0.2	-2.2	-2.4

Table S3. Calculated thiophene dihedral angles for **2SO_n**.

Compound	Dihedral Rings 1-2 (deg)	Dihedral Rings 2-3 (deg)
2S GS	11	15
2S ES	2	1
2S Δ(GS - ES)	9	14
2SO GS	24	6
2SO ES	1	0
2SO Δ(GS - ES)	23	6
2SO ₂ GS	11	7
2SO ₂ ES	3	2
2SO ₂ Δ(GS -ES)	8	5

Table S4. Calculated ground-state (GS) and excited-state (ES) bridging-sulfur (S) total bond orders (TBO) and their differences [Δ(ES – GS)] for **2SO_n**. The total bond order contains contributions between S and all other atoms in the molecule, largely the directly bonded C atoms and O in **2SO** and **2SO₂**.

Compound	TBO S-C Mayer	TBO S-C GJ	TBO S-C NM1	TBO S-C NM2	TBO S-C NM3
2S GS	2.3549	2.4404	2.7955	2.7925	2.7657
2S ES	2.4067	2.4904	2.8292	2.8302	2.7896
2S Δ(ES - GS)	0.0518	0.0500	0.0337	0.0377	0.0239
2SO GS	3.6671	3.3261	3.8114	4.0686	3.6786
2SO ES	3.6384	3.3058	3.8092	4.0633	3.6584
2SO Δ(ES - GS)	-0.0287	-0.0203	-0.0022	-0.0053	-0.0202
2SO ₂ GS	5.6543	4.4314	4.9053	6.0552	4.6458
2SO ₂ ES	5.6599	4.4284	4.9143	6.0545	4.6375
2SO ₂ Δ(ES - GS)	0.0113	0.0029	0.0090	-0.0021	0.0022

Table S5. Calculated ground-state (GS) and excited-state (ES) bridging-sulfur $\rightarrow$ carbon (**S-C**) bond orders (BO) and their differences [$\Delta(\text{ES} - \text{GS})$] for **2SO_n**.

Compound	BO S-C Mayer	BO S-C GJ	BO S-C NM1	BO S-C NM2	BO S-C NM3
2S GS	1.0647	1.0547	1.2038	1.2391	1.1970
2S ES	1.0759	1.0672	1.2077	1.2487	1.1972
2S $\Delta(\text{ES} - \text{GS})$	0.0112	0.0125	0.0039	0.0096	0.0002
2SO GS	0.8789	0.8852	0.9272	1.1132	0.8276
2SO ES	0.8799	0.8856	0.9354	1.1161	0.8281
2SO $\Delta(\text{ES} - \text{GS})$	0.0010	0.0004	0.0082	0.0029	0.0005
2SO ₂ GS	0.9377	0.8241	0.8176	1.2228	0.6916
2SO ₂ ES	0.9678	0.8410	0.8392	1.2344	0.7049
2SO ₂ $\Delta(\text{ES} - \text{GS})$	0.0301	0.0169	0.0216	0.0116	0.0133

Solvent Analysis

In equation 2, ε is the solvent dielectric constant and n is the refractive index of the solvent. The solvent polarity was adjusted by using binary mixtures of cyclohexane (CHx), dichloromethane (DCM), and acetonitrile (ACN) (Table 2).

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad \text{equation S2.}$$

For binary mixtures the dielectric constant and refractive index can be calculated using equations 3 and 4, where f is the volume fraction of solvent A or B.

$$\begin{aligned} \varepsilon_{AB} &= \varepsilon_A f_A + \varepsilon_B f_B \\ n_{AB} &= n_A f_A + n_B f_B \end{aligned} \quad \text{equations S3 and S4.}$$

Solvent vol. fraction	Δf
ACN	0.305
ACN ₈₀ /DCM ₂₀	0.296
ACN ₅₀ /DCM ₅₀	0.279
ACN ₂₀ /DCM ₈₀	0.253
DCM	0.218
DCM ₈₀ /CHx ₂₀	0.205
DCM ₅₀ /CHx ₅₀	0.172
DCM ₂₀ /CHx ₈₀	0.105
CHx	0

Table S6. Calculated Δf values for solvent mixtures used.

Figure S3. Lippard-Mattaga solvent-dependence analysis of series 2SO_n . (A-C) Change in absorbance ($\bullet$) and emission wavenumber ($\blacksquare$) as a function of the solvent polarity (Δf). (D) Change in Stokes shift for 2SO ($\blacklozenge$), 2SO_2 ($\blacktriangledown$). The above data yields changes in emission energy (slope of linear fit) as (A) - 0.13 (± 0.07), (B) -0.30 (± 0.10), and (C) -0.50 (± 0.10). Analysis of the data in (D) shows an increase in Stokes shift (slope of linear fit) for 2SO_2 (0.43 (± 0.06)), and 2SO (0.28 (± 0.12)).

Figure S4. Normalized emission spectra for **2S** (A), **2SO** (B), **2SO₂** (C), and terthiophene (D) showing the change in emission profile in increasingly polar solvents from non-polar CH_x (red) → ACN (black).

Figure S5. Full-width at half-maximum (FWHM) as a function of solvent polarity for **2S** (A), **2SO** (B), and **2SO₂** (C).

Figure S6. ^1H NMR spectrum of **1S**

^1H observe ref. to CDCl_3 at 7.27 ppm
CHLOROFORM-d
Frequency (MHz): 300.13

Figure S7. ^1H NMR spectrum of **1SO**

Figure S8. ^1H NMR spectrum of **1SO₂**

DICHLOROMETHANE- d_2
Frequency (MHz): 400.13

Figure S9. ^1H NMR spectrum of **2S**

Figure S10. ^1H NMR spectrum of 2SO

PRC2-043B.002.esp

Figure S11. ^1H NMR spectrum of 2SO₂

^1H
DICHLOROMETHANE- d_2
Frequency (MHz): 600.15

Figure S12. ^1H NMR spectrum of **3S**

^1H
DICHLOROMETHANE- d_2
Frequency (MHz): 600.15

Figure S13. HSQC spectrum of **3S**

5 mm Multinuclear inverse Z-grad Z8202/217
DICHLOROMETHANE-d2
Frequency (MHz): 400.13

Figure S14. ^1H NMR spectrum of 3SO

Figure S15. ^1H NMR spectrum of 3SO₂

Figure S16. ^1H NMR spectrum of **4S**

py-S-py.001.esp

Figure S17. HSQC spectrum of **4S**

Job no: 4315 Pete Christensen PRC Py-SO PRC Py-SO 1-1 1H ref to CD₂Cl₂ at 5.32 ppm
DICHLOROMETHANE-d₂
Frequency (MHz): 400.19

Figure S18. ¹H NMR spectrum of 4SO

Job no: 4315 Pete Christensen PRC Py-SO PRC Py-SO 1-1 1H ref to CD₂Cl₂ at 5.32 ppm
DICHLOROMETHANE-d₂
Frequency (MHz): 400.19

Figure S19. HSQC spectrum of 4SO

Figure S20. ^1H NMR spectrum of 4SO_2

Figure S21. Infrared spectra of 1SO_2 , 1SO and 1S .

Figure S22. Infrared spectra of 2SO_2 , 2SO and 2S .

Figure S23. Infrared spectra of 3SO_2 , 3SO and 3S .

Figure S24. Infrared spectra of 4SO_2 , 4SO and 4S .

Figure S25. Relative UV-VIS spectra for (A) 1S, 1SO, 1SO₂, (B) 2S, 2SO, 2SO₂, (C) 3S, 3SO, 3SO₂, (D) 4S, 4SO, 4SO₂. For comparison, the spectrum for each parent arene is also shown (—).

Figure S26. Absorbance corrected emission spectra for all compounds, including the parent arenes.

Table S7. Solid state Φ_f values.

Compound	Φ_f	Compound	Φ_f
1S	0.02	2S	0.07
1SO	0.00	2SO	0.12
1SO₂	0.18	2SO₂	0.08

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