Supporting Information

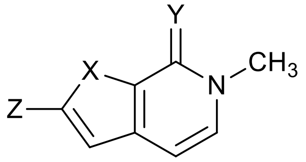
Room-temperature phosphorescence from small organic systems containing thiocarbonyl moiety

Chun-Hao Huang[a], Pei-Jhen Wu[b], Kun-You Chung[b], Yi-An Chen[b], Elise Y. Li[a],* and Pi-Tai Chou[b],*

[a]Department of Chemistry, National Taiwan Normal University, Taipei, 11677, Taiwan

[b]Department of Chemistry, National Taiwan University, Taipei, 10617, Taiwan

Contents



compound

SO : X = S ; Y = O

SS : X = S ; Y = S

OO : X = O ; Y = O

OS : X = O ; Y = S

SSI : X = S ; Y = S ; Z = I

SSBr : X = S ; Y = S ; Z= Br

Fig. S1 The chemical structures of **SO**, **SS**, **OO, OS**, **SSI** and **SSBr**.

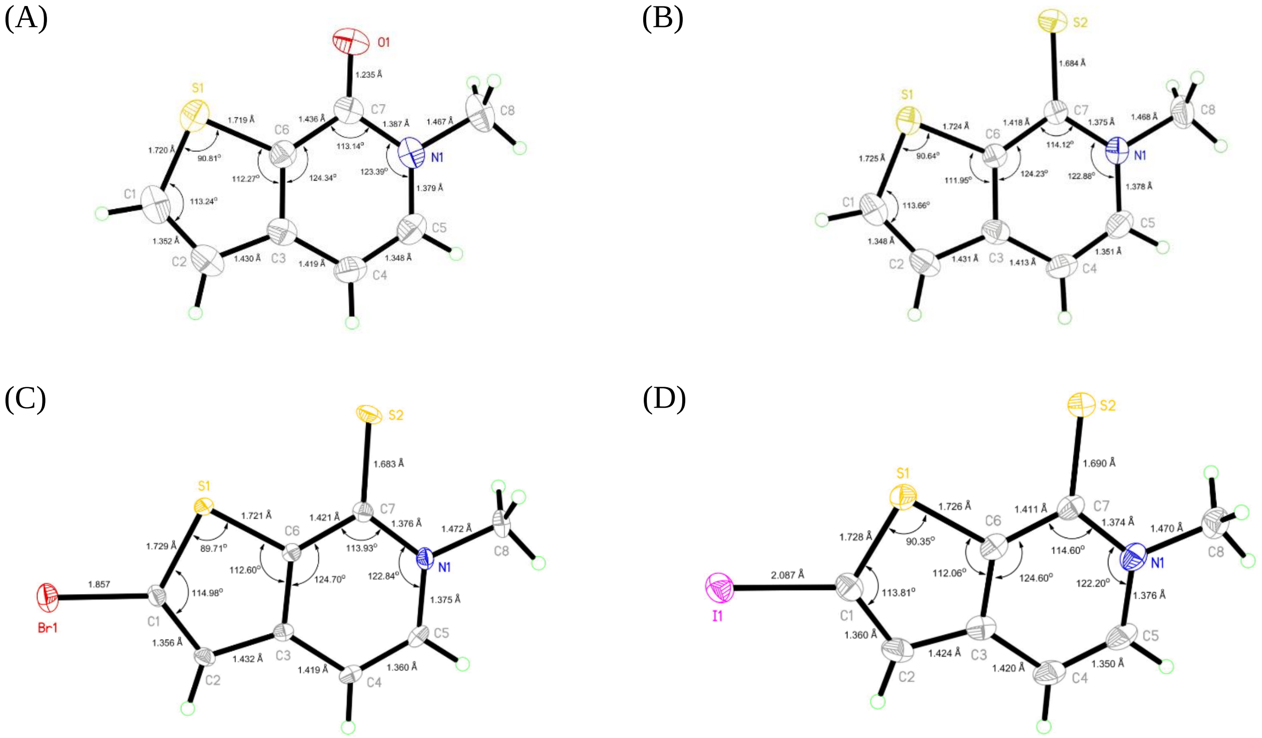
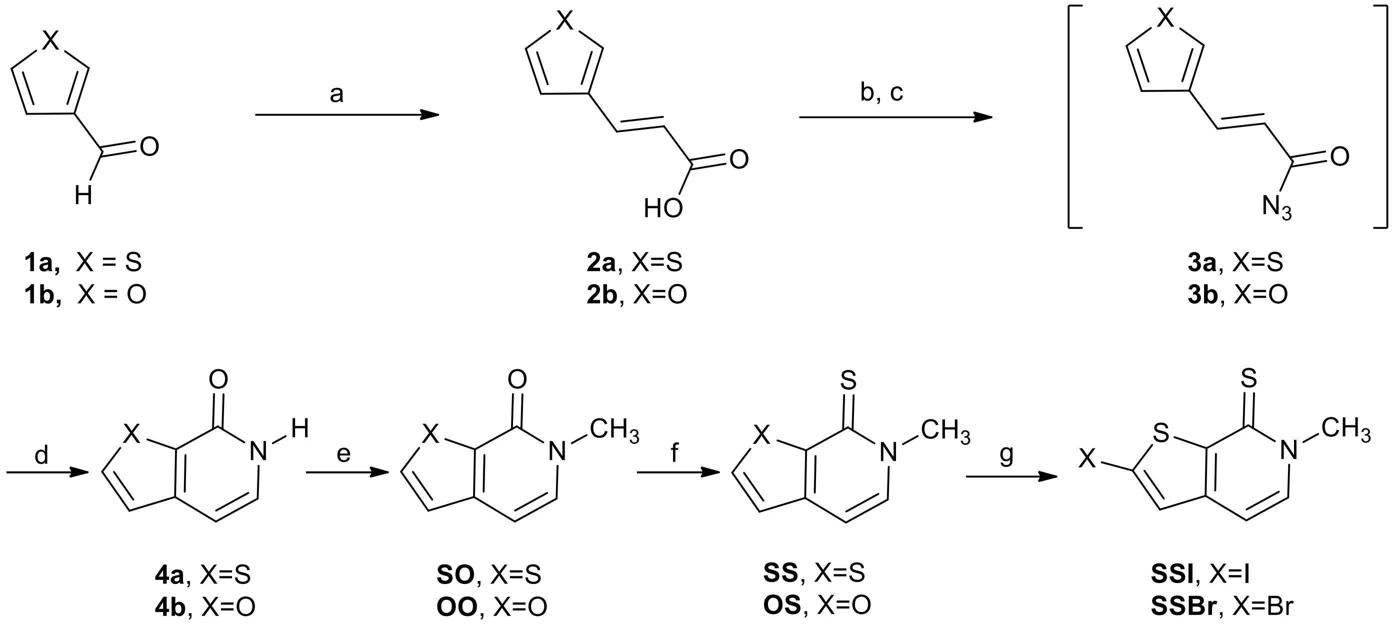


Fig. S2 The X-ray structures of (A) **SO** (B) **SS** (C) **SSBr** (D) **SSI** thermal ellipsoids drawn at 50% probability level.



Reagent (a) malonic acid, piperidine, pyridine; (b) thionyl chloride, chloroform, DMF or TEA, acetone, isobutyl chloroformate; (c) NaN_3, dioxane, H_2O; (d) diphenyl ether, tributylamine; (e) NaH, MeI; (f) Lawesson's reagent, toluene; (g) LDA, I_2 or LDA, 1,2-Dibromotetrachloroethane

Scheme S1. Synthetic routes for the compounds in this study.

Synthesis and Characterizations

All reactions were carried out in oven- or flame-dried glassware under a positive pressure of N_2. All reagents were purchased commercially and used without further purification. TLC was performed on Merck 5715 silica gel 60 F254 pre-coated plates. Flash column chromatography was carried out using silica gel from Merck (230-400 mesh). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Unity-400 MHz instrument. Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). MS data was obtained using a Shimadzu LCMS-IT-TOF Mass Spectrometer. Single-crystal X-ray diffraction data were acquired on a Bruker SMART CCD diffractometer using λ (Mo-Kα) radiation (λ = 0.71073 Å). The data collection was executed using the SMART program. Cell refinement and data reduction were carried out with the SAINT program. The structure was determined using the SHELXTL/PC program and refined using full-matrix least squares. All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed at calculated positions and included in the final stage of refinements with fixed parameters.

Synthesis of 3-(3-Thienyl)acrylic Acid (**2a**): A mixture of thiophene-3-carboxaldehyde (**1a**, 5 mL, 57 mmol) , malonic acid (7.7 g, 74.1 mmol) and piperidine (0.85 mL, 8.6 mmol) in pyridine was heated under reflux for 18 h. The reaction mixture was cooled to r.t., poured in to ice-water and acidified with $HCl_{(aq)}$. The crude product was filtered and washed with cold water to yield **2a** (8.31 g, 95%) as a white solid. ^{1}H NMR (400 MHz, DMSO): δ 7.91-7.92 (m, 1H), 7.49-7.59 (m, 3H), 6.33 (d, *J* = 16 Hz, 1 H). ^{13}C NMR (100 MHz, DMSO): δ 167.9, 137.8, 137.5, 129.1, 127.7, 125.7, 118.5. ESI-MS: m/z 154 (M^+).

Synthesis of 3-(3-Furyl)acrylic acid (**2b**): Compound **2b** was synthesized by similar procedures as described for compound **2a** except that **1b** was used instead of **1a**. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 12.19 (b, 1H), 8.05

(s, 1 H), 7.70 (s, 1 H), 7.47 (d, *J* = 16 Hz, 1H), 6.90 (s, 1H), 6.23 (d, *J* = 16 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.6, 145.4, 144.9, 134.4, 122.4, 118.7, 107.9. ESI-MS: m/z 138 (M^+).

Synthesis of Thieno[2,3-c]pyridin-7(6H)-one (**4a**): Thionyl chloride (2.8 mL, 38.4 mmol) was added to a solution of 3-(3-Thienyl)acrylic Acid (**2a**, 5.0 g, 32 mmol) in chloroform (25 mL). After refluxing for 2 h, the solution was concentrated under reduced pressure to get acyl chloride. The acyl chloride (4.8 g, 27.8 mmol) in dioxane was added dropwise to a solution of sodium azide (3.6 g, 55.6 mmol) in dioxane/water (1:1, 9 mL) at 0 °C. After stirring for 1 h, the organic layer was collected, dried over $MgSO_4$ and concentrated to give **3a**. Crude mixture of **3a** in CH_2Cl_2 was added dropwise to the mixture of diphenyl ether (20 mL) and tributylamine (3.5 mL) which had been heated to 220 °C over 1 h. After cooling to r.t., hexane was added to the mixture. The precipitates were collected by filtration, washed with water and dried to yield **4a** (1.82 g, 43%) as a brown solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.45 (s, 1H), 8.00 (d, *J* = 4.8 Hz, 1 H), 7.35 (d, *J* = 5.2 Hz, 1 H), 7.23 (d, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 6.8 Hz, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.5, 146.2, 133.7, 130.1, 129.1, 124.9, 102.2. ESI-MS: m/z 151 (M^+).

Synthesis of Furo[2,3-c]pyridin-7(6H)-one (**4b**): A mixture of **2b** (1.5 g, 10.9mmol), trimethylamine (1.8 mL, 13 mmol) and isobutyl chloroformate (1.9 mL, 14.2 mmol) in acetone (15 mL) was stirred at 0℃ for 0.5 h. After removing solvent, the residue in dioxane was added dropwise to a solution of sodium azide (1.1 g, 16.5 mmol) in dioxane/water at 0 °C and stirred for 1 h. The organic layer was collected, dried over anhydrous magnesium sulfate and concentrated to give **3b**. Crude mixture of **3b** in CH_2Cl_2 was added dropwise to the mixture of diphenyl ether and tributylamine which had been heated to 220℃ over 1 h. After cooling to r.t., hexane was added to the mixture. The precipitates were collected by filtration, washed with water and dried to yield **4b** as a brown solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.53 (s, 1H), 8.07 (d, *J* = 2 Hz, 1 H), 7.13 (d, *J* = 7.2 Hz, 1 H), 6.86 (d, *J* = 1.6 Hz, 1H), 6.00 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.0, 148.8, 143.0, 133.6, 129.4, 107.6, 99.6. ESI-MS: m/z 135 (M^+).

Synthesis of 6-methylthieno[2,3-c]pyridin-7(6H)-one (**SO**): To a solution of **4a** (4.0 g, 26.4 mmol) in THF at 0 °C was added NaH (60%, 1.3 g, 31.7 mmol) and stirred. After1 h, iodomethane (2.0 mL) was added and stirred overnight. The reaction mixture was concentrated and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered and evaporated. The residue was purified by silica gel column chromatography with CH_2Cl_2/EtOAc mixture as eluent to afford **SO** (2.5 g, 57%) as an amber solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 5.2 Hz, 1H), 7.16 (d, *J* = 4.8 Hz, 1 H), 7.14 (d, *J* = 7.2 Hz, 1 H), 6.60(d, *J* = 6.8 Hz, 1H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 145.2, 133.6, 133.2, 130.3, 124.1, 102.9, 36.7. ESI-MS: m/z 165 (M^+).

Synthesis of 6-methylfuro[2,3-c]pyridin-7(6H)-one (**OO**): Compound **OO** was synthesized by similar procedures as described for compound **SO** except that **4b** was used instead of **4a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 2.4 Hz, 1H), 7.09 (d, *J* = 6.8 Hz, 1 H), 6.62 (d, *J* = 6.8 Hz, 1 H), 6.43 (d, *J* = 2 Hz, 1H), 3.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 148.0, 143.6, 132.8, 132.6, 107.1, 100.0, 36.5. ESI-MS: m/z 149 (M^+).

Synthesis of 6-methylthieno[2,3-c]pyridine-7(6H)-thione (**SS**): A solution of **SO** (3.0 g, 18.1 mmol), Lawesson's reagent (4.4 g,10.9 mmol) and dry toluene (200 mL) was refluxed overnight. After cooling to r.t., the reaction mixture was concentrated, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and evaporated. The residue was purified by silica gel column chromatography with EtOAc/Hexane mixture as eluent to yield **SS** (1.4 g, 43%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 5.2 Hz, 1H), 7.57 (d, *J* = 6.8 Hz, 1 H), 7.24 (d, *J* = 5.6 Hz, 1 H), 7.00 (d, *J* = 6.8 Hz, 1H), 4.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.3, 145.5, 139.3, 137.3, 135.5, 124.4, 108.7, 44.8. ESI-MS: m/z 181 (M^+).

Synthesis of 6-methylfuro[2,3-c]pyridine-7(6H)-thione (**OS**): Compound **OS** was synthesized by similar procedures as described for compound **SS** except that **OO** was used instead of **SO**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 2 Hz, 1H), 7.56 (d, *J* = 6.4 Hz, 1 H), 6.85 (d, *J* = 6.4 Hz, 1 H), 6.72 (d, *J* = 2 Hz, 1H), 4.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 154.5, 150.5, 135.5, 127.6, 107.3, 105.8, 44.1. ESI-MS: m/z 165 (M^+).

2-bromo-6-methylthieno[2,3-c]pyridine-7(6H)-thione (**SSBr**): To a solution of **SS** (0.3 g, 1.7 mmol) in THF under N_2 at -78℃ was added dropwise with lithium diisopropylamide (1.1 mL, 2.2 mmol) and stirred for 1 h. The mixture then treated with1,2-dibromotetrachloroethane (0.72 g, 2.2 mmol), warm to room temperature and stir overnight. After quenched with water, the organic solvent was then removed in vacuo, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and evaporated. The residue was purified by silica gel column chromatography with CH_2Cl_2/Hexane mixture as eluent to yield **SSBr** (0.29 g, 66%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.2 Hz, 1H), 7.23 (s, 1 H), 6.89 (d, *J* = 6.8 Hz, 1 H), 4.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 139.5, 136.1, 127.3, 126.6, 123.5, 107.7, 44.7. ESI-MS: m/z 258 (M^+).

2-iodo-6-methylthieno[2,3-c]pyridine-7(6H)-thione (**SSI**): To a solution of **SS** (0.3 g, 1.7 mmol) in THF under N_2 at -78℃ was added dropwise with lithium diisopropylamide (1.1 mL, 2.2 mmol) and stirred for 1 h. The mixture then treated with Iodine (0.56 g, 2.2 mmol), warm to room temperature and stir overnight. After quenched with sodium hydrogen sulfite, the organic solvent was removed in vacuo, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and evaporated. The residue was purified by silica gel column chromatography with CH_2Cl_2/Hexane mixture as eluent to yield **SSI** (0.36 g, 70%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 6.8 Hz, 1H), 7.45 (s, 1 H), 6.91 (d, *J* = 7.2 Hz, 1 H), 4.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 150.6, 140.2, 135.9, 134.3, 107.1, 90.5, 44.5. ESI-MS: m/z 306 (M^+).

Table S1. Crystal data and structure refinement for **SO**.

Empirical formula	C8 H7 N O S	
Formula weight	165.21	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 10.0478(3) Å	a= 90°.
	b = 10.3511(3) Å	b= 90°.
	c = 14.6556(5) Å	g = 90°.
Volume	1524.27(8) Å^3	
Z	8	
Density (calculated)	1.440 Mg/m^3	
Absorption coefficient	0.357 mm^{-1}	
F(000)	688	
Crystal size	0.200 x 0.180 x 0.120 mm^3	
Theta range for data collection	2.780 to 27.484°.	
Index ranges	-12<=h<=13, -13<=k<=12, -18<=l<=19	
Reflections collected	9737	
Independent reflections	1747 [R(int) = 0.0189]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.7102	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1747 / 0 / 101	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0298, wR2 = 0.0794	
R indices (all data)	R1 = 0.0346, wR2 = 0.0831	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.228 and -0.327 e.Å^{-3}	

Table S2. Crystal data and structure refinement for **SS**.

Empirical formula	C8 H7 N S2	
Formula weight	181.27	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2$_1$/c	
Unit cell dimensions	a = 7.0250(3) Å	a= 90°.
	b = 8.6002(4) Å	b= 100.7881(17)°.
	c = 13.5237(6) Å	g= 90°.
Volume	802.61(6) Å^3	
Z	4	
Density (calculated)	1.500 Mg/m^3	
Absorption coefficient	0.588 mm^{-1}	
F(000)	376	
Crystal size	0.180 x 0.150 x 0.050 mm^3	
Theta range for data collection	2.821 to 27.497°.	
Index ranges	-9<=h<=9, -11<=k<=11, -17<=l<=17	
Reflections collected	6215	
Independent reflections	1841 [R(int) = 0.0181]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7462 and 0.7044	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1841 / 0 / 101	
Goodness-of-fit on F^2	1.102	
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0807	
R indices (all data)	R1 = 0.0390, wR2 = 0.0831	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.302 and -0.234 e.Å^{-3}	

Table S3. Crystal data and structure refinement for **SSBr**.

Empirical formula	C8 H6 Br N S2	
Formula weight	260.17	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.9208(3) Å	a= 85.0711(17)°.
	b = 7.5423(4) Å	b= 82.0272(16)°.
	c = 8.8756(5) Å	g = 89.0243(17)°.
Volume	457.11(4) Å^3	
Z	2	
Density (calculated)	1.890 Mg/m^3	
Absorption coefficient	4.891 mm^{-1}	
F(000)	256	
Crystal size	0.310 x 0.140 x 0.110 mm^3	
Theta range for data collection	2.711 to 27.482°.	
Index ranges	-8<=h<=8, -9<=k<=9, -11<=l<=11	
Reflections collected	4025	
Independent reflections	2099 [R(int) = 0.0090]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5731	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2099 / 0 / 110	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0241, wR2 = 0.0682	
R indices (all data)	R1 = 0.0257, wR2 = 0.0688	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.441 and -0.801 e.Å^{-3}	

Table S4. Crystal data and structure refinement for **SSI**.

Empirical formula	$C_8H_6INS_2$	
Formula weight	307.16	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.3765(2) Å	a= 90°.
	b = 18.9914(7) Å	b= 118.0593(13)°.
	c = 7.7127(3) Å	g = 90°.
Volume	953.47(6) Å^3	
Z	4	
Density (calculated)	2.140 Mg/m^3	
Absorption coefficient	3.738 mm^{-1}	
F(000)	584	
Crystal size	0.250 x 0.080 x 0.080 mm^3	
Theta range for data collection	2.145 to 27.495°.	
Index ranges	-9<=h<=9, -24<=k<=24, -10<=l<=9	
Reflections collected	6979	
Independent reflections	2186 [R(int) = 0.0237]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.6545	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2186 / 0 / 110	
Goodness-of-fit on F^2	1.105	
Final R indices [I>2sigma(I)]	R1 = 0.0207, wR2 = 0.0450	
R indices (all data)	R1 = 0.0267, wR2 = 0.0465	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.369 and -0.797 e.Å^{-3}	

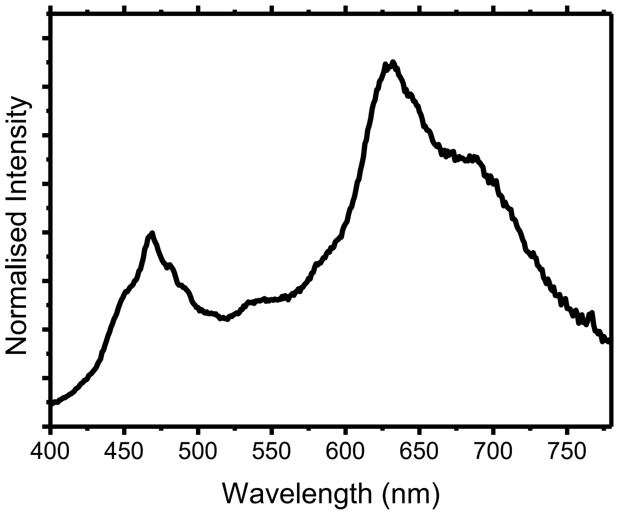


Fig. S3 The solid state emission spectra of **SS** (λ_{ex} = 355 nm). The overall quantum yield was determined to be 0.07.

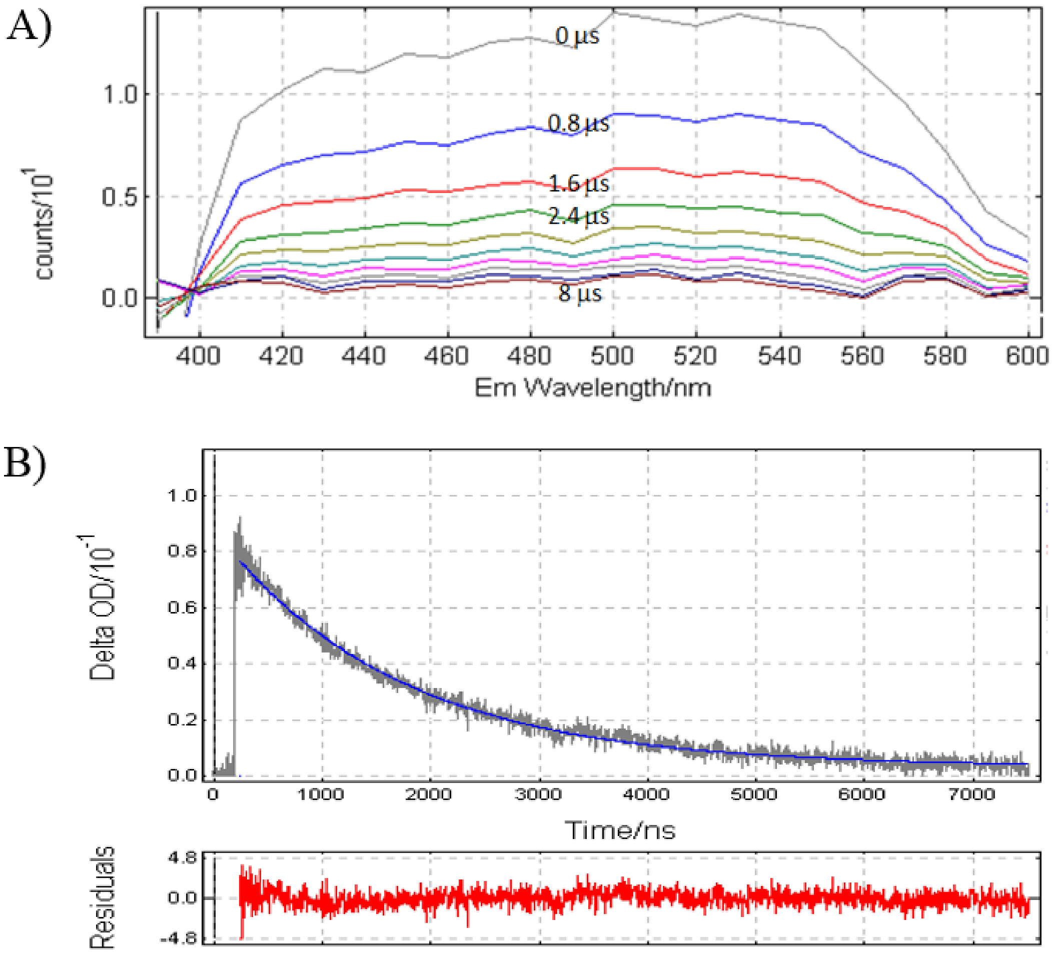


Fig. S4. (A)The transient absorption spectrum of SS in degassed DCM solution at different time delay; gray: 0 us, blue: 0.8 ms, red: 1.6 ms, green: 2.4 ms, brown: 8 ms. (B) The time-dependent relaxation dynamics of SS in degassed DCM solution monitored at 540 nm. The fitted lifetime was 1758 ns.

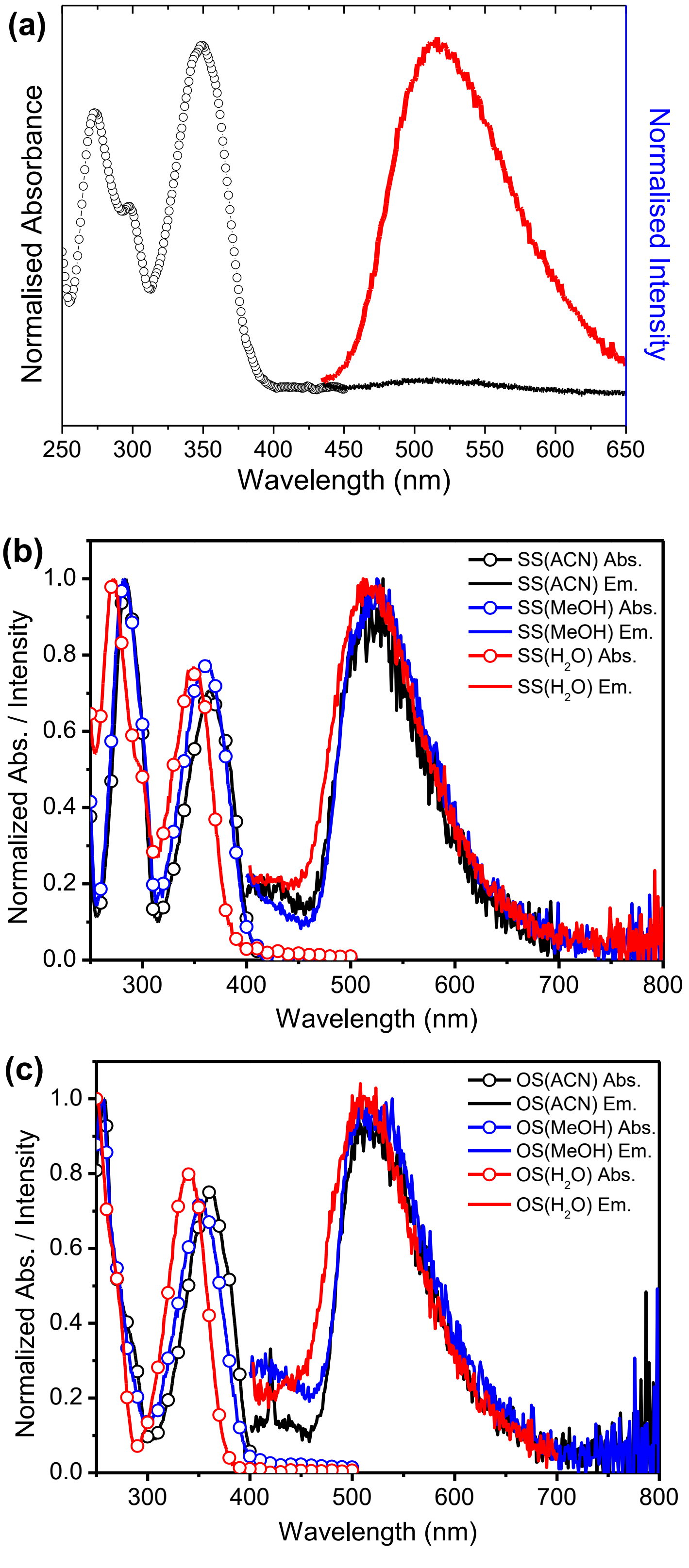


Figure S5. (**a**) The steady state absorption (black circle) and emission spectra of **SS** in aerated H_2O (black line) and degassed H_2O (red line), respectively. Note that the emission at < 430 nm was cut by inserting a > 420 nm long-wavelength passed filter. Normalized steady-state absorption (dotted line) and emission (solid line) for (b) **SS** and (c) **OS** in different degassed solvents at room temperature. ACN: acetonitrile, MeOH: methanol.

Table S5. Calculated bond lengths and bond angles of the optimized $\mathbf{S_0}$ geometry of **SO**, **SS**, **SSBr** and **SSI**

	SO	SS	SSBr	SSI
d(C$_1$-C$_2$) (Å)	1.36	1.36	1.35	1.37
d(C$_2$-C$_3$) (Å)	1.43	1.43	1.43	1.43
d(C$_3$-C$_4$) (Å)	1.42	1.42	1.42	1.43
d(C$_4$-C$_5$) (Å)	1.35	1.35	1.35	1.36
d(C$_6$-C$_7$) (Å)	1.44	1.42	1.43	1.43
d(N$_1$-C$_5$) (Å)	1.37	1.37	1.37	1.39
d(N$_1$-C$_7$) (Å)	1.39	1.37	1.38	1.39
d(N$_1$-C$_8$) (Å)	1.46	1.46	1.46	1.47
d(S$_1$-C$_1$) (Å)	1.72	1.72	1.74	1.75
d(S$_1$-C$_6$) (Å)	1.72	1.72	1.73	1.74
d(Y-C$_7$) (Å)	1.23 (Y=O$_1$)	1.69 (Y=S$_2$)	1.68 (Y=S$_2$)	1.68 (Y=S$_2$)
d(Z-C$_1$) (Å)	---	---	1.87 (Y=Br$_1$)	2.08 (Z=I$_1$)
$\angle$C$_1$-S$_1$-C$_6$	90.6°	90.7°	89.5°	89.9°
$\angle$C$_2$-C$_1$-S$_1$	113.3°	113.6°	114.6°	113.5°
$\angle$C$_3$-C$_6$-S$_1$	112.4°	111.9°	112.5°	112.6°
$\angle$C$_3$-C$_6$-C$_7$	123.8°	123.8°	124.3°	124.9°
$\angle$C$_6$-C$_7$-N$_1$	113.4°	114.4°	113.6°	113.4°
$\angle$C$_7$-N$_1$-C$_5$	123.4°	123.0°	123.1°	123.1°

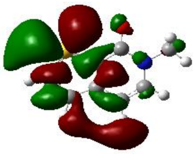
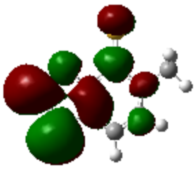
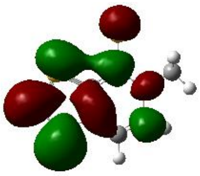
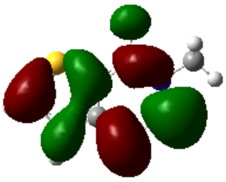
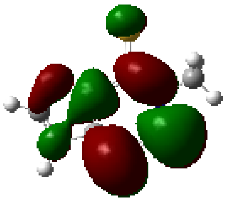
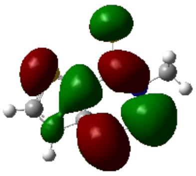
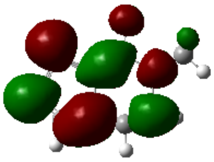
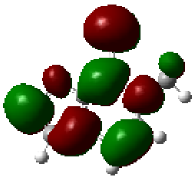
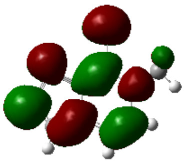
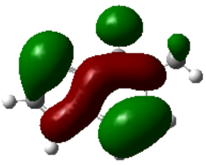
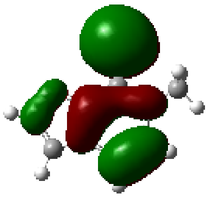
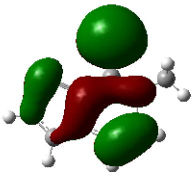
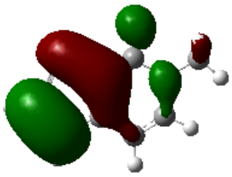
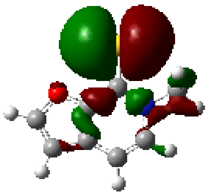
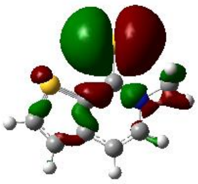
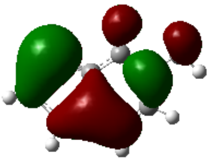
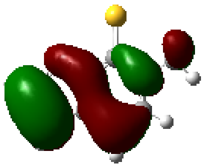
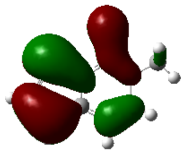
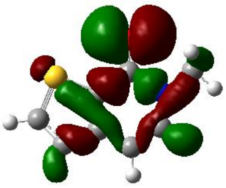
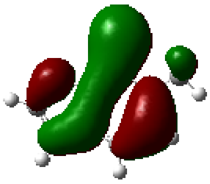
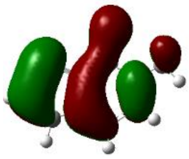
MO	SO	OS	SS
LUMO+2	 1.66 eV	 1.73eV	 1.38 eV
LUMO+1	 0.65 eV	 0.3 eV	 0.08 eV
LUMO	 -0.49 eV	 -0.8 eV	 -0.98 eV
HOMO	 -7.31 eV	 -7.07 eV	 -7.09 eV
HOMO-1	 -8.43 eV	 -7.47eV	 -7.5 eV
HOMO-2	 -9.23 eV	 -8.59 eV	 -8.26 eV
HOMO-3	 -9.47 eV	 -9.63 eV	 -9.1 eV

Fig. S6 Calculated molecular orbitals at the optimized ground state geometry at the M062X/TZP level.

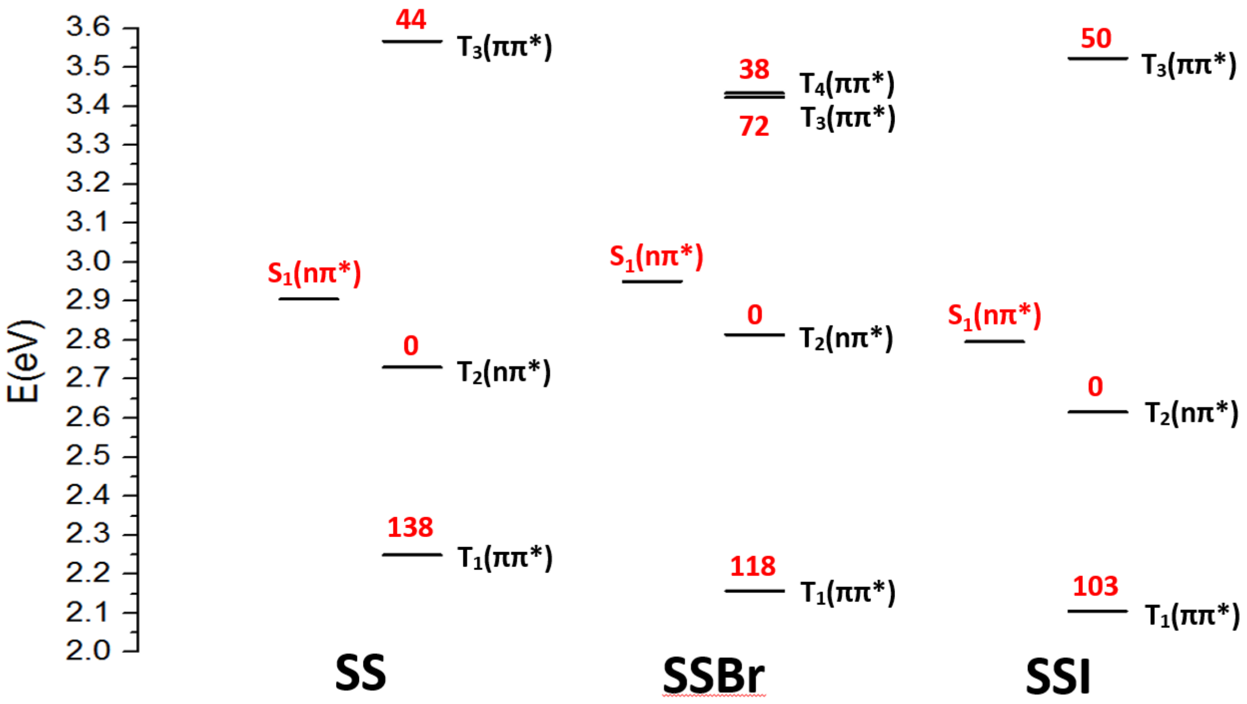


Fig. S7 The singlet and triplet excited state energies and major excitation characteristics for **SS** derivatives in the optimized S_1 geometry. Numbers in red denote the SOC integrals between S_1 and various triplet states (cm^{-1}) calculated with the full Breit-Pauli operator.[17]

Table S6. Theoretical absorption and luminescence data measured in DCM

	$E(S_1)@S_0$ (eV, nm)	f	$E(S_1)@S_1$ (eV, nm)	f	$[E(T_1)]@T_1$ (eV, nm)	$f(T_1)$
SO	(4.45, 278.6)	0.198	(3.80, 326.5)	0.192	(1.86, 667)	0.88E-8
OS	(3.57, 347.3)	0	(3.34, 371.1)	0	(2.31, 536)	0.33E-4
SS	(3.56, 347.9)	0	(3.32, 373.8)	0	(2.18, 569)	0.93E-8

Table S7. Calculated excitation energy and oscillator strengths of the low-lying electronically excited states at the optimized $\mathbf{S_1}$ geometry of **SO**

SO	Energy (eV)	contribution	Oscillator strength
T_1 (ππ*)	2.64	H → L (95.9%)	--
S_1 (ππ*)	3.8	H → L (97.2%)	0.192
T_2 (ππ*)	3.82	H → L+1 (49.8%)	--
T_3 (ππ*)	3.88	H-1 → L (52.2%)	--
T_4 (ππ*)	4.61	H-2 → L (74.4%)	--
S_2 (ππ*)	5.01	H-1 → L (55%)	0.0232
T_5 (nπ*)	5.06	H-3 → L (72.2%)	--
S_3 (nπ*)	5.3	H-3 → L (52.2%)	0.0017

Table S8. Calculated excitation energy and oscillator strengths of the low-lying electronically excited states at the optimized **S_1** geometry of **SS**

SS	Energy (eV)	contribution	Oscillator strength
T_1 (ππ*)	2.6	H → L (95%)	--
T_2 (nπ*)	3.17	H-1 → L (89.5%)	--
S_1 (nπ*)	3.32	H-1 → L (91%)	0
T_3 (ππ*)	3.57	H-2 → L (89.8%)	--
S_2 (ππ*)	3.66	H → L (97.3%)	0.236
T_4 (ππ*)	3.8	H → L+1 (68.2%)	--

Table S9. Calculated low-lying triplet excited states at the optimized **T_1** geometry of **SS** with the inclusion of relativistic effects

SS	Energy (eV)	Contribution	Oscillator strength
S_1 (ππ*)	3.24	H → L (96.7%)	0.43
T_1 (ππ*)	2.18	H → L (91.8%)	0.93E-8
T_2 (ππ*)	2.37	H-2 → L (27.5%)	0.24E-8
T_3 (ππ*)	3.06	H-2 → L (43.3%)	0.21E-7
T_4 (nπ*)	3.27	H-1 → L (87.7%)	0.78E-1