Supplementary Information

Selenium Substitution Enhances Reverse Intersystem Crossing in a Delayed Fluorescence Emitter

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<u>Synthesis</u>

All reagents were used as received from Sigma-Aldrich. Microwave reactions were conducted in sealed vials in a Biotage Initiator synthetic microwave.

2-bromo-9*H*-thioxanthen-9-one (TXO-Br)

14 mL of bromobenzene was added to 200 mL of sulphuric acid, followed portion-wise by 5 g of thiosalicylic acid. After stirring at room temperature for 24 hours, the solution was heated to 70 °C for 90 minutes, then cooled and poured over ice. The precipitate was extracted with DCM and purified using column chromatography (ether) to give 4.08 g of an orange solid (45%). ¹H NMR (400 mHz, CDCl₃) δ 8.70 (d, J = 1.9 Hz, 1H), 8.61-8.54 (m, 1H), 7.67 (dd, J = 8.6 Hz, 1H), 7.55 (m, 2 H), 7.49-7.40 (m, 2H).

2-bromo-9*H*-thioxanthen-9*H*-one 10-oxide (TXO₁-Br)

408 mg of TXO-Br and 266 mg of mCPBA were dissolved in 150 ml DCM at 0 °C and stirred for 12 hours. The solution was washed with saturated Na2SO4 and NaHCO3 solutions then purified by column chromatography (DCM) to give 166 mg of a white powder (27%).¹H NMR (400 mHz, CDCl₃) δ 8.48 (d, J = 2.0, 1H), 8.36 (dd, J = 7.3, 1H), 8.16 (d, J = 7.7 Hz, 1H), 8.03 (d, J = 8.3 Hz, 1H) 7.96 (dd, J = 8.3 Hz, 1H), 7.87 (td, J = 7.8 Hz, 1H), 7.74 (td, J = 7.6, 1H). TOF- MS (DART +) m/z 308.9 [M + H]⁺.

2-(4-(diphenylamino)phenyl)-9*H*-thioxanthen-9-one 10-oxide (TXO₁-TPA)

80 mg of bromothioxanthenone, 120 mg of triphenylamine boronic acid, 80 mg of K2CO3, and 32 mg of Pd XPhos were added to a 5 ml microwave vial and put under vacuum for 1 hour. A mixture of 2 ml of ethanol and 1 ml of water was bubbled with argon for 1 hour before being added to the solids. The vial was put in the microwave at 105 °C for 1 hour then cooled and opened to air. The organic products were extracted using DCM, and the product was purified using column chromatography (gradient DCM to EtOAc) to give 120 mg of an orange solid (98%). ¹H NMR (400 mHz, CDCl₃) δ 8.57 (d, J = 1.9 Hz, 1H), 8.40 (dd, J = 7.8 Hz, 1H), 8.22-8.17 (m, 2H), 8.04 (dd, 8.2 Hz, 1H), 7.87 (td, J = 7.8, 1H), 7.74 (td, J = 7.6, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.32-7.27 (m, 4H), 7.18-7.14 (m, 6H), 7.08 (t, J = 7.2, 2H). TOF- MS (DART +) *m*/z 472.1 [M + H]⁺.

4-Chlorobenzeneselenol

70 mL of THF was added to 1.2 g of crushed magnesium turnings under nitrogen. A spatula tip of catalytic iodine was added followed by 9.5 g of 1-bromo-4-chlorobenzene. The Grignard was allowed to form under reflux for 30 minutes or until the magnesium turnings were no longer being consumed then 1.2 g of selenium powder was added. After reacting for 30 minutes, the mixture was poured over ice. Concentrated HCl was added to remove residual magnesium, and the precipitated product was extracted with ether. The solvent was removed to give an odorous yellow solid which was used immediately (5.5 g, 58%). ¹H NMR (400 mHz, CDCl₃) δ 7.53-7.49 (m, 2H), 7.26-7.22 (m, 2H).

2-((4-chlorophenyl)selanyl)benzoic acid

75 mL of water was added to 6 g of KOH, followed by 300 mg of copper powder and 8.7 g of 2iodobenzoic acid. The mixture was stirred at 40 °C for 20 minutes then 6.7 g of 4chloroselenophenol was added. After refluxing for 7 hours, the mixture was cooled and poured over ice. The product was precipitated with concentrated HCl and filtered before being recrystallized in ethanol to give a tan solid (4.8 g, 87%). TOF- MS (DART +) m/z 312.9 [M + H]⁺.

2-chloro-9H-selenoxanthen-9-one (SeXO-Cl)

5 mL of sulphuric acid was heated to 95 °C and 1 g of Step 2 was added slowly over 20 minutes. After 90 minutes, the solution was poured over ice to precipitate the product as a yellow solid. It was then extracted with ether, the solvent was removed, and the product was recrystallized in a 1:1 mixture of ethanol and benzene to give a yellow solid (680 mg, 78%). ¹H NMR (400 mHz, CDCl3) δ 8.62-8.66 (m, 2H), 7.46-7.66 (m, 5H). ⁷⁷Se NMR (500 mHz, CDCl₃) δ 337.7. TOF-MS (DART +) *m*/z 294.9 [M + H]⁺.

2-(4-(diphenylamino)phenyl)-9*H*-selenoxanthen-9-one (SeXO-TPA)

100 mg of SeXO-Cl, 120 mg of triphenylamine boronic acid, 120 mg of K2CO3, and 36 mg of Pd XPhos were added to a 5 ml microwave vial and put under vacuum for 1 hour. A mixture of 3 ml of ethanol and 1 ml of water was bubbled with argon for 1 hour before being added to the solids. The vial was put in the microwave at 105 °C for 2 hours then cooled and opened to air. The organic products were extracted using DCM, and the product was purified using column chromatography (DCM:hexanes 1:1) to give 166 mg of an orange solid (97%). ¹H NMR (400 mHz, CDCl₃) δ 8.87 (d, J = 2.2 Hz, 1 H), 8.67 (dd, J = 7.9 Hz, 1H), 7.77 (dd, J = 8.3 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.65 (dd, J = 7.7 Hz, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.9 Hz, 1H), 7.28 (t, J = 7.3 Hz, 4H), 7.16 (t, J = 7.2 Hz, 6H), 7.05 (t, J = 7.0 Hz, 2H). ⁷⁷Se NMR (500 mHz, CDCl₃) δ 331.8. TOF- MS (DART +) *m/z* 504.1 [M + H]⁺.

2-(4-(diphenylamino)phenyl)-9*H*-selenoxanthen-9-one 10-oxide (SeXO₁-TPA)

11.5 mg of SeXO-TPA were dissolved in 10 ml of DCM and cooled in an ice bath. 7 mg of mCPBA were added and the reaction was stirred overnight at room temperature. The mixture was washed with aqueous Na₂CO3, and the solvent was removed to give 11.8 mg of an orange solid (99%). ¹H NMR (400 mHz, CDCl₃) δ 8.58 (d, J = 2.0, 1 H), 8.41 (dd, J = 7.8, 1H), 8.10 (d, J = 8.1, 2H), 7.98 (dd, J = 8.1, 1H), 7.82 (t, J = 7.6, 1H), 7.74 (t, J = 7.6, 1H), 7.54 (d, J = 8.9, 2H), 7.29 (t, J = 8.5 4H), 7.15 (m, 6H), 7.07 (t, 2H). ⁷⁷Se NMR (500 mHz, CDCl₃) δ 800.1. TOF-MS (DART +) *m*/*z* 520.1 [M + H]⁺.

¹H and ¹³C NMR spectra of new compounds



Figure S1. ¹H NMR (top) and ¹³C NMR (bottom) of 2-(4-(diphenylamino)phenyl)-9*H*-selenoxanthen-9-one (400 mHz, CDCl₃).



Figure S2. ¹H NMR (top) and ¹³C NMR (bottom) of 2-(4-(diphenylamino)phenyl)-9*H*-selenoxanthen-9-one 10-oxide (400 mHz, CDCl₃).



180 178 176 174 172 170 168 166 164 162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 f1 (ppm)

Figure S3. ¹H NMR (top) and ¹³C NMR (bottom) of 2-bromo-9*H*-thioxanthen-9-one 10-oxide (400 mHz, CDCl₃).



Figure S4. ¹H NMR (top) and ¹³C NMR (bottom) of 2-(4-(diphenylamino)phenyl)-9*H*-thioxanthen-9-one 10-oxide (400 mHz, CDCl₃).

Density functional theory calculations

Methods

All quantum-chemistry calculations were performed using the Gaussian 16 suite of programs. Geometry optimizations for the ground and excited states were performed using density functional theory (DFT) and time-dependent DFT with the LC- BLYP functional¹ and the 6-31+G(d) basis set within the Tamm–Dancoff approximation.² The range-separated parameters for the LC-BLYP functional were optimized for each molecule to incorporate a reasonable amount of exact exchange (0.170 and 0.175 Bohr⁻¹ for TXO₁-TPA and SeXO₁-TPA, respectively).³ The corrected linear response polarizable continuum model for toluene was used to include the solvation effect on the excited states.⁴ Spin–orbit coupling (SOC) matrix elements were calculated by using the Breit–Pauli Hamiltonian with an effective charge approximation implemented in the PySOC program.⁵

Results

Table S1. Energetics and oscillator strength from density functional calculations

Compound	Еномо ^{<i>a</i>} (eV)	ELUMO b (eV)	E _{S1@S0} ^c (nm, eV)	f@80 ^d	E _{T1@S0} ^e (nm, eV)
TXO ₁ -TPA	-6.56	-1.38	404, 3.07	0.109	456, 2.72
SeXO ₁ -TPA	-6.60	-1.34	394, 3.15	0.113	446, 2.78

^{*a*}Energy of the highest occupied molecular orbital. ^{*b*}Energy of the lowest unoccupied molecular orbital. ^{*c*}Energy and ^{*d*}oscillator strength of the S₀ to S₁ vertical transition. ^{*e*}Energy of the S₀ to T₁ vertical transition.

	S1 geometry		T1 geometry		
Compound	$\langle S_1 \widehat{H_{SO}} T_1 \rangle$	$\langle S_1 \widehat{H_{SO}} T_2 \rangle$	$\langle S_1 \widehat{H_{SO}} T_1 \rangle$	$\langle S_1 \widehat{H_{SO}} T_2 \rangle$	
TXO ₁ -TPA	0.807 cm^{-1}	4.58 cm^{-1}	0.63 cm ⁻¹	0.42 cm^{-1}	
SeXO ₁ -TPA	1.28 cm ⁻¹	9.12 cm ⁻¹	0.80 cm^{-1}	1.44 cm ⁻¹	

Table S2. Spin orbit coupling matrix elements in the S1 and T1 geometries calculated from DFT

Experimental methods

All solvents were used as received from Sigma-Aldrich, except acetonitrile, which was dried using an Innovative Technology solvent purification system and stored in an argon-filled glovebox (mBraun).

Time-resolved PL spectra were recorded using an electrically-gated intensified charge-coupled device (ICCD) camera (Andor iStar DH740 CCI-010) connected to a calibrated grating spectrometer (Andor SR303i). Pulsed 400 nm photoexcitation was provided at a repetition rate of 1 kHz. A 425 nm long-pass filter (Thorlabs) was used to prevent scattered laser signal from entering the camera. Temporal evolution of the PL emission was obtained by stepping the ICCD gate delay with respect to the excitation pulse. The minimum gate width of the ICCD was 5 ns. Recorded data was subsequently corrected to account for filter transmission and camera sensitivity.

Transient absorption (TA) measurements were performed on a home-built TA setup, powered by a Ti:sapphire amplifier (Spectra Physics Solstice Ace) that generated 100 fs duration pulses centred at 800 nm, with a repetition rate of 1 kHz. On this setup, sample photoexcitation in the short-time TA experiments (100 fs - 1.7 ns) was achieved by the second harmonic (400 nm;

fluence = $63.5 \,\mu$ J/cm²) of the 800 nm output of the Ti:sapphire amplifier, generated using a β-Barium Borate (BBO) crystal and filtered with a BG39 glass filter to remove the residual fundamental pulse. For long time measurements (1 ns – 1 µs), the third harmonic (355 nm; fluence = $4.98 \,\mu$ J/cm² for TXO₁-TPA and $3.85 \,\mu$ J/cm² for SeXO₁-TPA) of an electronically triggered, Q-switched Nd:YVO4 (1 ns pump length, Advanced Optical Technologies Ltd AOT-YVO-25QSPX) was used. The probe light was generated by home-built broadband visible (500 – 770 nm) and near-infrared ($830 - 1025 \,$ nm) non-collinear optical parametric amplifiers (NOPAs), pumped using the 400 nm second harmonic of the Ti:sapphire output. For short-time measurements, a mechanical delay stage (Thorlabs DDS300-E/M) was used provide the pumpprobe delay. In the long-time measurements, the delay between probe and pump pulses was varied using a Stanford DG645 delay generator. The transmitted probe pulses were collected with a silicon dual-line array detector (Hamamatsu S8381-1024Q) which was driven and read out by a custom-built board from Stresing Entwicklungsbüro.

Measurement of transient CW EPR (trEPR) was done in the Centre for Advanced ESR (CAESR) in the Department of Chemistry of the University of Oxford, using a Bruker BioSpin EleXSys I E680 at X-band, 9.7 GHz, with an ER 4118X-MD5W resonator. Temperature was controlled with an Oxford Instruments CF935O cryostat under liquid helium flow and an ITC-503S controller. An Opotek Opolete HE355 LASER was used for optical excitation of the samples and it was synchronised to the spectrometer by a Stanford Research DG645 delay generator. Use of a Stanford Research SR560 low-noise preamplifier of the CW Mode signal at 3-300 kHz was in substitute of the video amplifier, following verification against the DC-AFC Transient Mode of 20 MHz bandwidth setting. Data was processed with MatLab (The Mathworks, Natick, N.J.), and ESR simulations made use of the EasySpin routines.⁶

All electrochemical measurements were performed in an argon-filled glovebox (mBraun) with oxygen and moisture levels less than 2 ppm, using a BioLogic SP-200 Potentiostat/Galvanostat/ Frequency Response Analyzer. All reported potentials are referenced to ferrocene. Cyclic voltammetry measurements were performed in a custom-made Teflon cell using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆)/acetonitrile electrolyte, with a platinum button working electrode, a platinum mesh counter electrode and a silver wire pseudoreference electrode. A scan rate of 50 mV/s was used for all measurements. An active material concentration of ~0.1 mM was used for both TXO₁-TPA and SeXO₁-TPA.

Photophysics

Solvatochromism



Figure S5. Photoluminescence of (A) SeXO₁-TPA and (B) TXO₁-TPA at 0.1 mg/ml in deoxygenated: toluene (blue), chlorobenzene (orange), and tetrahydrofuran (green).



Singlet-triplet energy gap

Figure S6. Fluorescence (blue) and phosphorescence (red) of SeXO₁-TPA at 0.1 mg/ml in deoxygenated toluene. The energetic onset of each reveals the singlet (¹CT) and triplet (³CT) energies. Comparing these energies we find $\Delta E_{ST} = 0.24$ eV.

Oxygen quenching



Figure S7. Photoluminescence of SeXO₁-TPA at 0.1 mg/ml in deoxygenated toluene (solid line) and exposed to an ambient environment (dashed). Comparing the integrated counts of each demonstrates that oxygen quenched emission contributes to 24% of total emission.

Table S3. Photoluminescence quantum efficiency and measured lifetimes

Compound	Φ ^a (%)	$\tau_{\rm ISC} \ ^{b}$ (ns)	$ au_{\mathrm{PF}} c$ (ns)	$ au_{ ext{triplet}} {}^{d} (\mu s)$	$ au_{\mathrm{DF}} e(\mu s)$
TXO ₁ -TPA	25	21.9	13	2.2	2.5
SeXO ₁ -TPA	1.5	0.085	< 0.14	0.8	0.7

^{*a*}Photoluminescence quantum efficiency (\pm 5%) measured in an integrating sphere, ^{*b*}intersystem crossing lifetime from TA (\pm 4 ns and \pm 1 ps, respectively). ^{*c*}Prompt fluorescence lifetime from exponential fit to TCSPC (\pm 0.6 ns for TXO₁-TPA, only upper bound stated for SeXO₁-TPA due to instrument limitation). ^{*d*}Triplet decay lifetime from TA (\pm 100 ns and \pm 14 ns, respectively). ^{*e*}Delayed fluorescence lifetime (\pm 100 ns) from exponential fit to ICCD. All measurements were taken in deoxygenated toluene.

Electron spin resonance spectroscopy

trESR of SeXO₁-TPA and TXO₁-TPA, was collected at a temperature of 10 K and microwave power of 0.2 mW, for 12 and 2 hrs of averaging respectively. Data represents time-average of the initial rise of the EPR signal, 1-2µs. Replacement of the S atom with Se more than doubles the apparent axial zero-field splitting of the triplet state signals in the trESR data, shown in Fig. S6. For the overall zero field splitting, eq. S4, there are spin-spin dipolar contributions and spin orbit contributions, eq. S5.

$$\hat{H}_{ZFS} = \hat{S} \cdot \boldsymbol{D} \cdot \hat{S} \tag{S1}$$

The zero field splitting tensor, D, is traceless and it may be described in an axial term D and orthorhombic term E, as in $D = D_{zz} - (D_{xx} - D_{yy})/2$ and $E = (D_{xx} - D_{yy})/2$, respectively. Simulation of the trESR spectrum of TXO₁-TPA gives a |D| value of approximately 2.1 GHz and simulation of the trESR spectrum from SeXO₁-TPA leads to a |D| value of at least 5 GHz.

The consequence of Se substitution is to increase the spin-orbit coupling contribution to the zerofield splitting, with spin-orbit coupling being proportional to atomic number $Z(I_n)$ shown in the following.

$$\widehat{H}_{SO} = \frac{\alpha^2}{2} \left[\sum_{i_e, I_n} \frac{Z(I_n)}{r_{i_e, I_n}^3} \widehat{L}_{i_e, I_n} \widehat{S}_{i_e} - \sum_{i_e, j_e} \frac{1}{r_{i_e, j_e}^3} \widehat{L}_{i_e, I_n} (\widehat{S}_{i_e} + \widehat{S}_{j_e}) \right]$$
(S2)

Here the fine structure constant is α , \hat{L} and \hat{S} are the operators for orbital angular momentum and spin angular momentum, respectively. These results demonstrate the contribution of Se to the zero field splitting, while in-depth ESR characterization, including high-field trESR, isotopic enrichment and ENDOR, is the subject of future studies.



Figure S8. (A) Electron spin resonance spectra of SeXO₁-TPA (top, green) and TXO₁-TPA (bottom, grey) at 0.2 mM frozen in toluene at 10 K. ESR data (top) and simulation (bottom) of (B) SeXO₁-TPA and (C) TXO₁-TPA. The ESR simulation zero field splitting tensor values D and E are shown.

Cyclic Voltammetry



Figure S9. Cyclic voltammetry of (A) TXO₁-TPA and (B) SeXO₁-TPA in 0.1 M

TBAPF₆/acetonitrile electrolyte, referenced to the ferrocene/ferrocenium redox couple.

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