Supporting Information

Crystallization Induced Room-Temperature Phosphorescence and Chiral Photoluminescence Properties of Phosphoramides

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Experimental Section

Materials

The chemicals were purchased from commercial suppliers (Aldrich, USA; Merck, Germany; SDFCL, India) and used as received unless otherwise mentioned. Standard Schlenk-line technique was used for reactions. THF was dried over sodium and distilled out under an argon atmosphere.

Methods

^{1}H, ^{31}P spectra were recorded at -90°C to 25 °C on a Bruker Avance 500 MHz NMR Spectrometer operating at a frequency of 500 MHz for ^{1}H and 200 MHz for ^{31}P. ^{1}H NMR spectra were referenced to TMS (0.00 ppm) as an internal standard. Chemical shift multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). ^{31}P NMR chemical shift values were referenced to the external standard phosphorous signal of 85% H_3PO_4. High-resolution mass spectra (HRMS) were recorded on a Micromass Q-ToF High-Resolution Mass Spectrometer by electrospray ionization (ESI) method. High-performance liquid chromatogram (HPLC) were recorded in The Waters Alliance 2695 Separation Module using a C18 column and 240 nm UV detector with acetonitrile/H_2O as eluent. Electronic absorption spectra, fluorescence emission spectra, and time-resolved fluorescence (TRF) decay measurements were recorded on a SHIMADAZU UV-2600 spectrophotometer and FLS-980 EDINBURGH spectrometer. Solutions of all the compounds for spectral measurements were prepared using anhydrous spectrophotometric grade solvents and standard volumetric glassware. Quartz cuvettes with sealing screw caps were used for the solution state spectral measurements. Single crystal X-ray diffraction studies were carried out with a Bruker SMART APEX diffractometer equipped with 4-axis goniometer for all the compounds. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL software. For compound **TPTZPO**, some disorder solvent molecules are present in the crystal lattice, which could not be modelled. Hence, those have been removed using PLATON/SQUEEZE program by taking their corresponding scattering contribution into account.

Unpolarised photoluminescence (PL) and CPL spectroscopy

The PL and CPL spectra of the samples were recorded in the solid powder states using a JASCO CPL-300 spectrofluoropolarimeter at 25 °C (scattering angle: 0°). The samples were excited using unpolarized monochromatic incident light. The excitation wavelengths were 360 nm. The bandwidth for all samples was 10 nm. A scanning speed of 50 nm/min was maintained and the PMT time constant was 8 s. The path length was 0.1 mm.

Computational calculations

All the calculations are performed in Gaussian 09 software in gas phase.[1] The optimization of **TPTZPO, TPTZPS**, and **TPTZPSe** performed in the ground (S_0) state using DFT with B3LYP functional 631-G(d, p) basis set and first excited singlet (S_1) and triplet states (T_1) by using TDDFT methods in combination with CAM-B3LYP functional 631-G(d, p) basis set by freezing all three P-N bonds.[2,3] The vertical transition energies calculated for S_0 to S_1 transition and energy of higher triplet states up to T_{15} was also calculated.

Gutowsky-Holm equation:

Free energies of activation ($\Delta G^{\#}$) can be obtained by solving Eyring's equation.

$\Delta G^{\#} = RT_c \ln(\sqrt{2}kT_c/h\pi\Delta\delta) = 0.00457T_c(9.97 + \log (T_c/\Delta\delta))$

Where, $\Delta\delta$ = Maximum difference between the two peaks at low temperature

T_c = Coalescence temperature

Experimental Section

General Synthetic Procedure

n-BuLi was added dropwise to an anhydrous THF solution of phenothiazine in a predried 250 mL RB at −78 °C under stirring conditions. The resultant reaction mixture was stirred at −78 °C for 1 h, followed by the addition of appropriate equivalence of PCl_3. The reaction mixture was stirred for 30 minutes at -78 °C, and the reaction temperature was slowly raised to 25 °C; and the stirring was continued for additional 12 h. Then, the reaction mixture was quenched with water and the organics were extracted with dichloromethane. The combined dichloromethane solutions were stored over anhydrous

$MgSO_4$ to remove water. Removal of organic volatiles under reduced pressure gave the crude product. The crude product was dissolved in CH_2Cl_2/ toluene and 30 % aqueous H_2O_2 (0°C, 3 h) / sulfur powder (20°C, 12 h) / selenium powder (20°C, 12 h) were added to obtain the oxidized/ sulfurized/ selenized products. Pure compound was obtained after silica gel column chromatography purification using hexane as an eluent.

Synthesis of tris-phenothiazinephosphine oxide (TPTZPO):

TPTZPO was prepared following the procedure as described above. The quantities involved and characterization data are as follows. Phenothiazine (2.0 g, 10.0 mmol), n-BuLi (7.5 mL, 12.0 mmol), PCl_3 (0.26 mL, 3.0 mmol), and 30 % aqueous H_2O_2 (10 mL). Yield: 1.74 g, 27%. m.p. = 192-195 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): Broad signal (7.0 ppm- 8.0 ppm) at room temperature and multiplets (6.5 ppm- 8.3 ppm) at -90°C. ESI-MS (m/z): calculated for $C_{36}H_{24}N_3OPS_3$, exact mass (M+Na): 664.0717; found (M+Na): 664.0718. Elemental analysis (%) for $C_{36}H_{24}N_3OPS_3$: C 67.37, H 3.77, N 6.55, S 14.99; found: C 67.76, H 4.34, N 6.49, S 15.19.

Synthesis of tris-phenothiazinephosphine sulfide (TPTZPS):

TPTZPS was prepared following the above general synthetic procedure. The quantities involved and characterization data are as follows. Phenothiazine (2.0 g, 10.0 mmol), n-BuLi (7.5 mL, 12.0 mmol), PCl_3 (0.26 mL, 3.0 mmol), and sulfur powder (400 mg). Yield: 1.5 g, 24%. ^{1}H NMR at -90°C (400 MHz, $CDCl_3$, ppm): δ 8.41 (m, 2H), δ 7.72 (t, 2H), δ 7.43 (m, 6H), δ 7.18 (m, 6H), δ 7.01 (d, 1H), δ 6.71 (d, 5H), δ 6.59 (d, 1H), δ 5.91 (d, 1H). ESI-MS (m/z): calculated for $C_{36}H_{24}N_3PS_4$, exact mass (M+Na): 680.0488; found (M+Na): 680.0489. Elemental analysis (%) for$C_{36}H_{24}N_3PS_4$: C 65.73, H 3.68, N 6.39, S 19.50; found: C 66.14, H 3.71, N 6.13, S 19.47.

Synthesis of tris-phenothiazinephosphine selenide (TPTZPSe): TPTZPSe was prepared following the above general synthetic procedure. The quantities involved and characterization data are as follows. Phenothiazine (0.5 g, 2.5 mmol), n-BuLi (2.0 mL, 3.0 mmol), PCl_3 (0.06 mL, 0.8 mmol), and selenium powder (300 mg). Yield: 0.45 g, 25%. ^{1}H NMR at -90°C (400 MHz, $CDCl_3$, ppm): δ 8.61 (d, 1H), δ 8.40 (dd, 2H), δ 7.93 (d, 1H), δ 7.71 (d, 1H), δ 7.42 (m, 7H), δ 7.11 (m, 6H), δ 6.65 (m, 4H), δ 6.54 (t, 1H), δ 5.89 (d, 1H). ESI-MS (m/z): calculated for $C_{36}H_{24}N_3PS_3Se$, exact mass (M+Na):

727.9933; found (M+Na): 727.9936. Elemental analysis (%) for $C_{36}H_{24}N_3PS_3Se$: C 61.36, H 3.43, N 5.96, S 13.65; found: C 61.80, H 3.67, N 5.72, S 13.85

Structural Characterizations

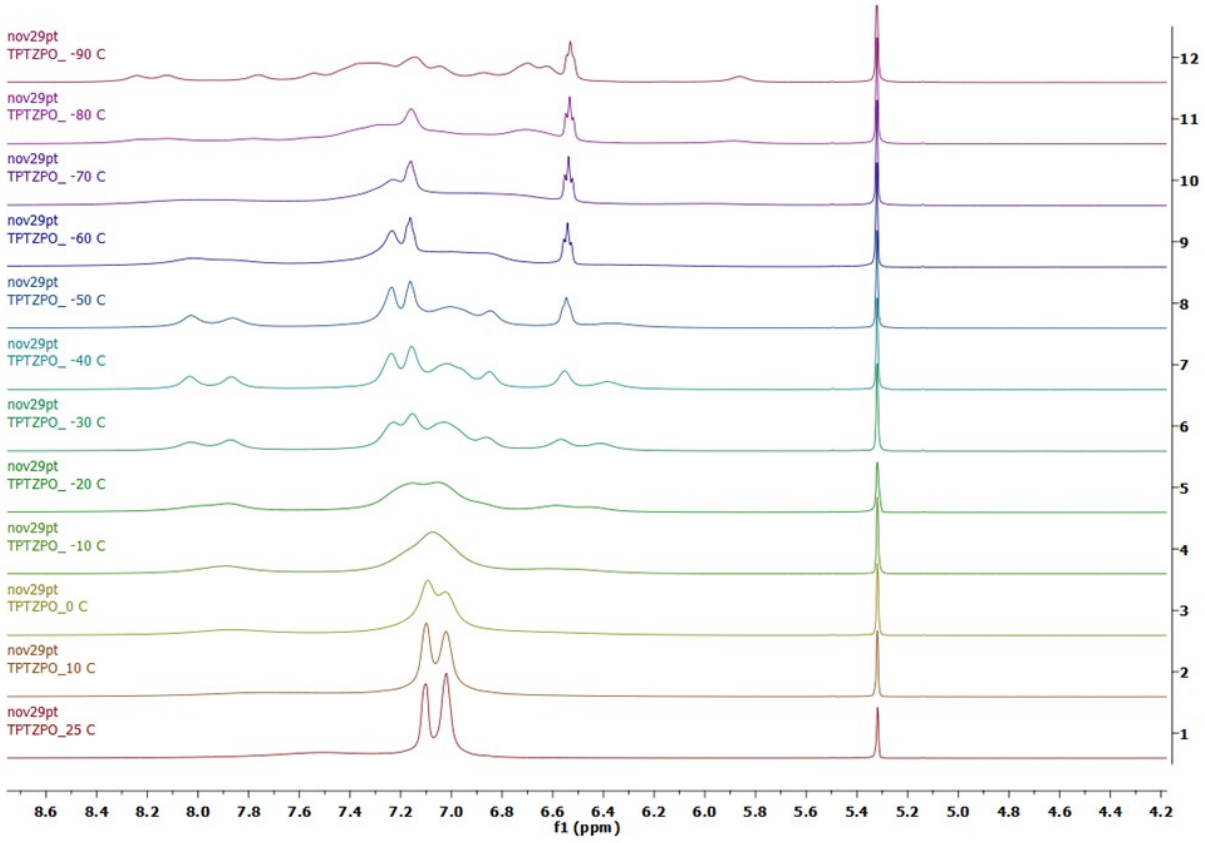


Figure S1: Variable temperature ^{1}H NMR spectra of compound **TPTZPO** in the range 25°C to -90°C (10 °C intervals) in CD_2Cl_2.

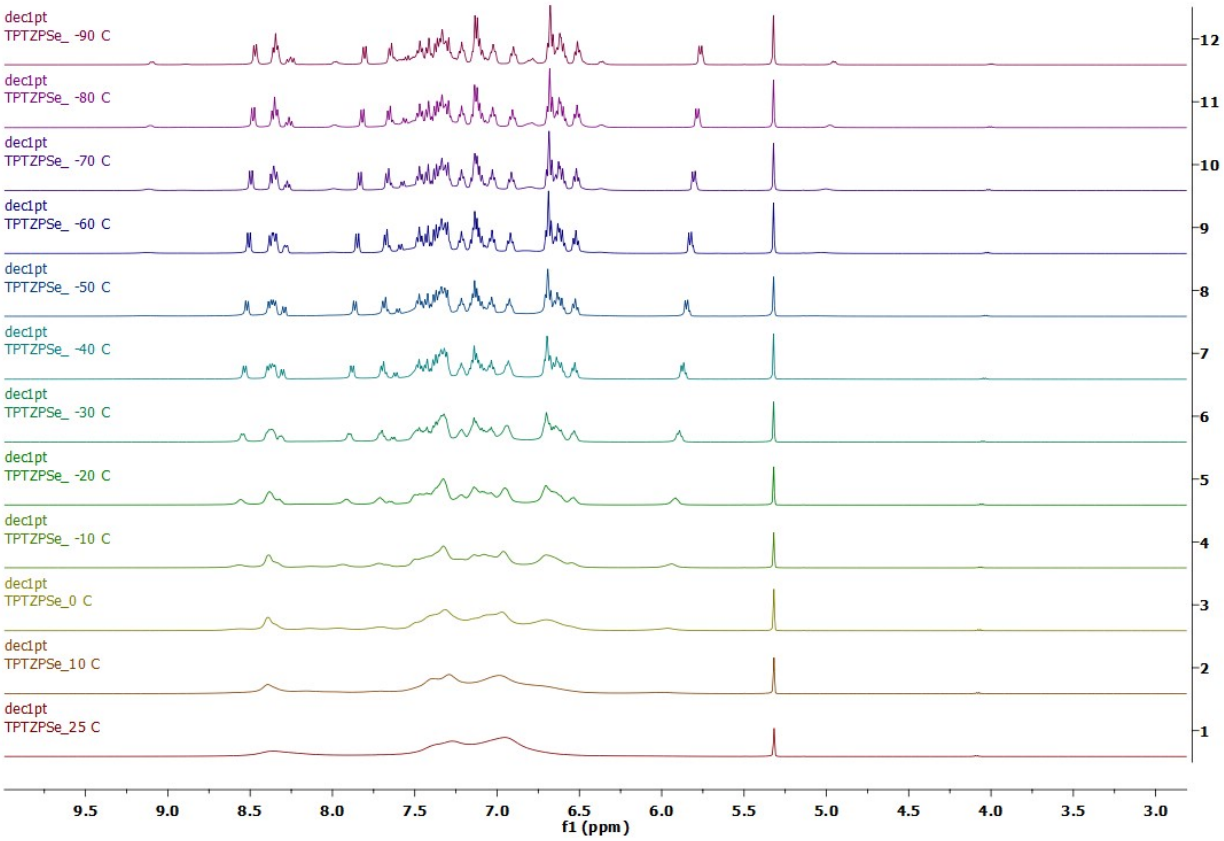


Figure S2: Variable temperature ^{1}H NMR spectra of compound **TPTZPSe** in the range 25°C to -90°C (10 °C intervals) in CD_2Cl_2.

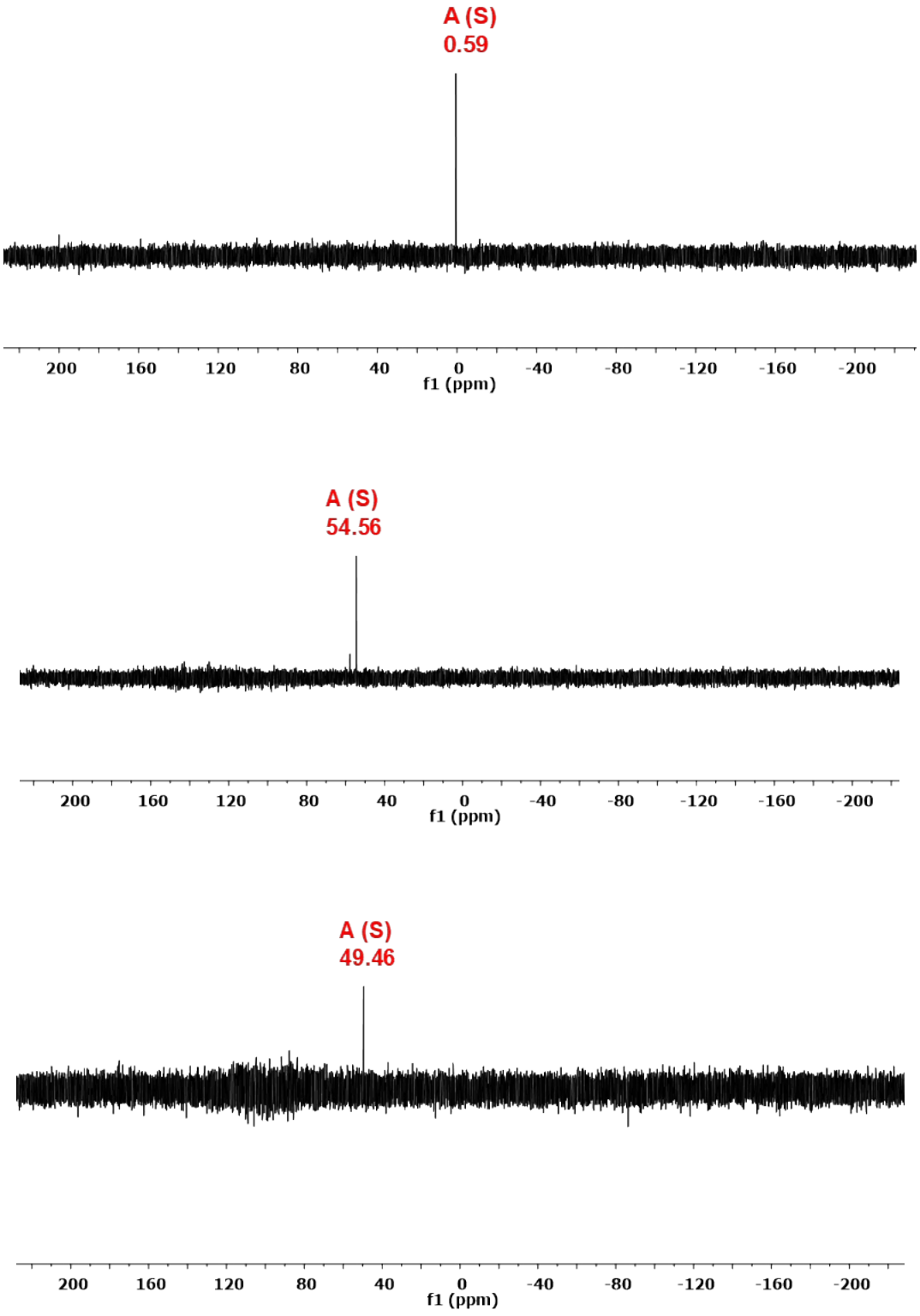


Figure S3: ^{31}P NMR spectra of compound **TPTZPO**(top), **TPTZPS** (middle) and **TPTZPSe** (bottom) in CD_2Cl_2.

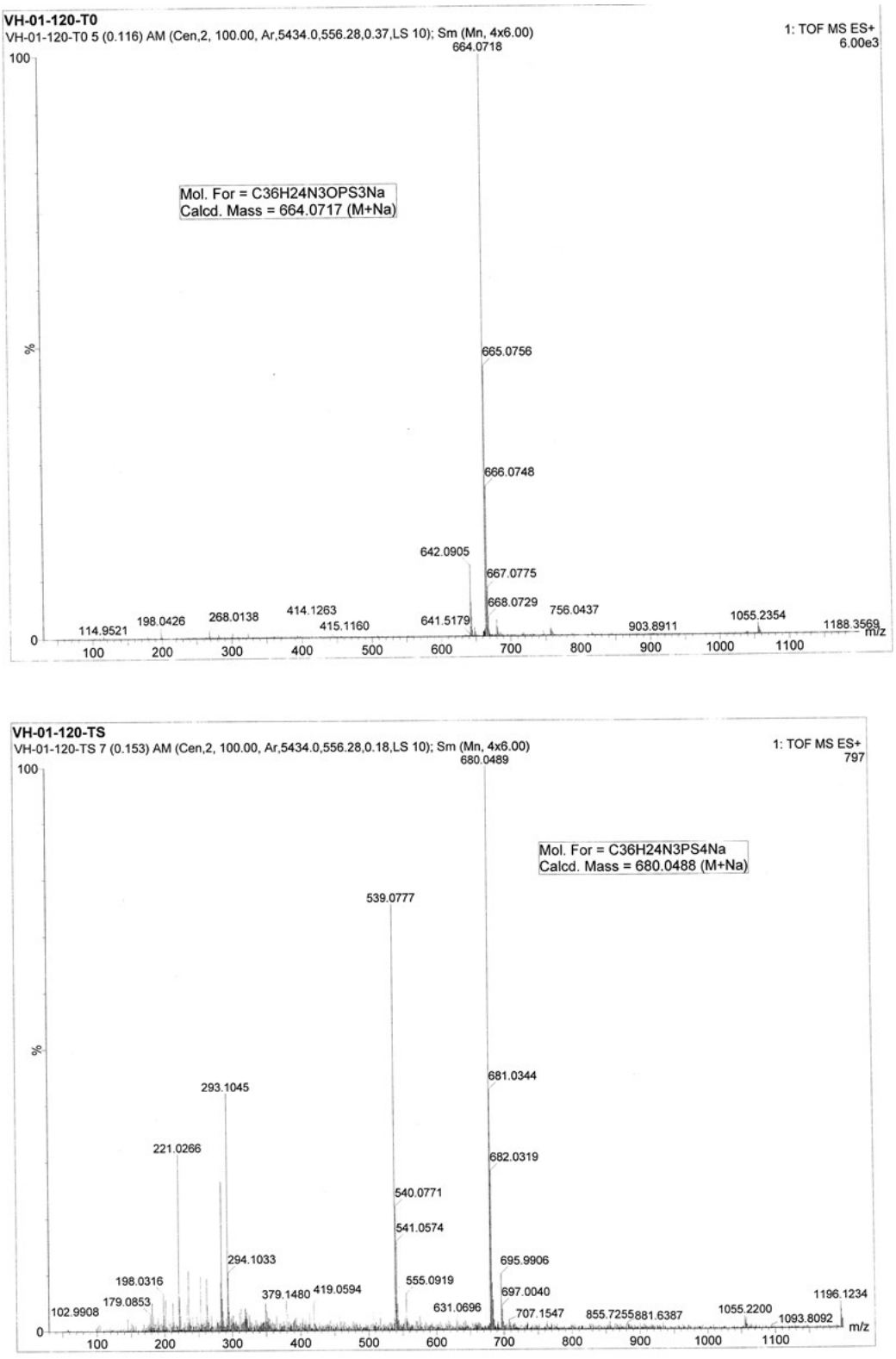


Figure S4: HRMS of compound **TPTZPO**(top) and **TPTZPS** (bottom).

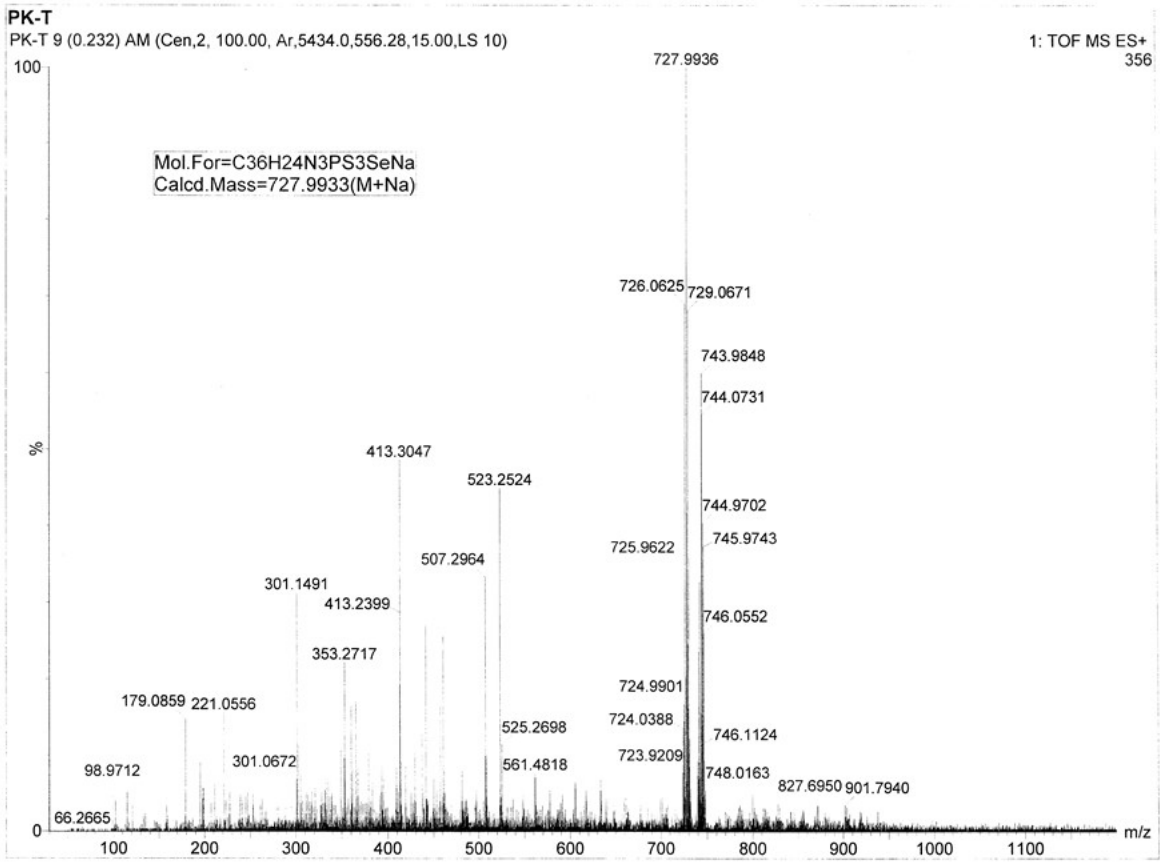


Figure S5: HRMS of compound **TPTZPSe.**

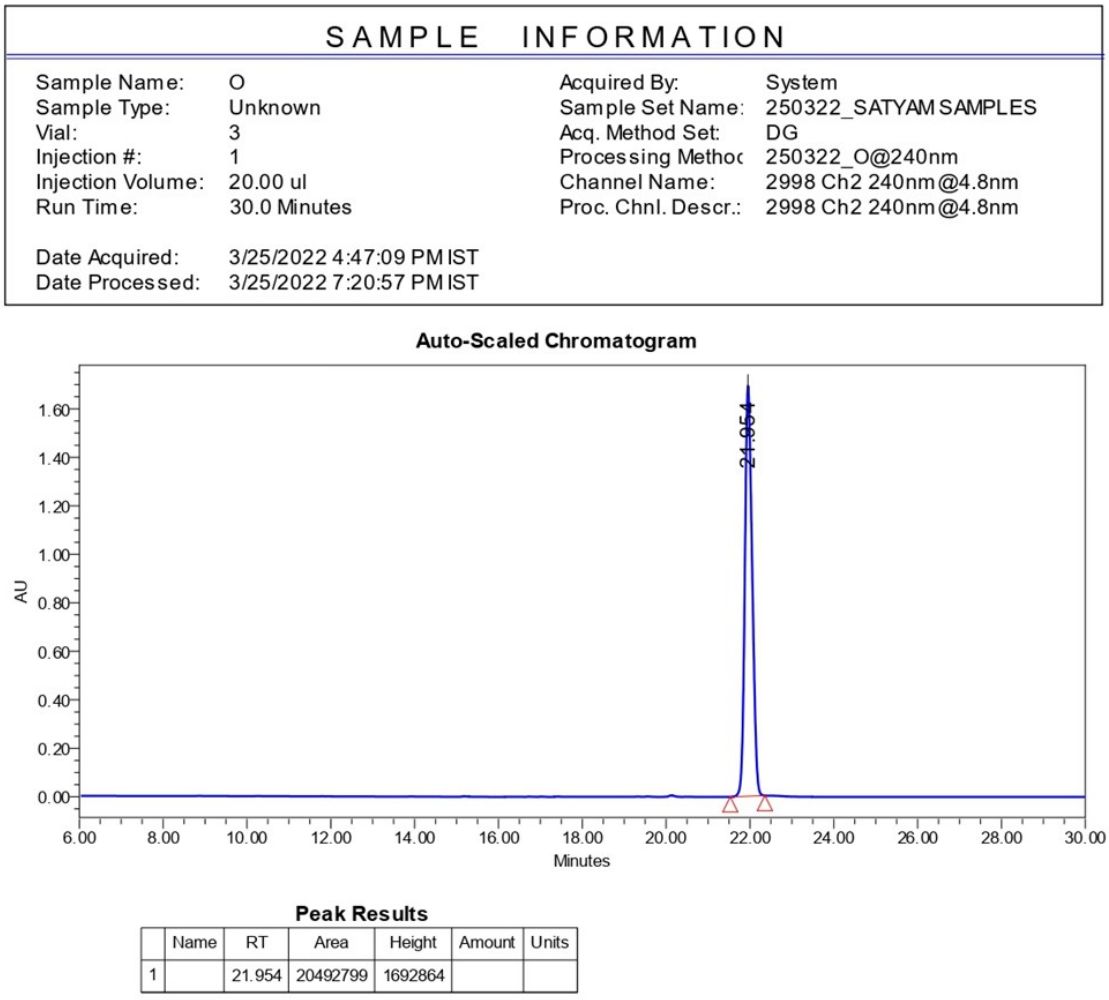
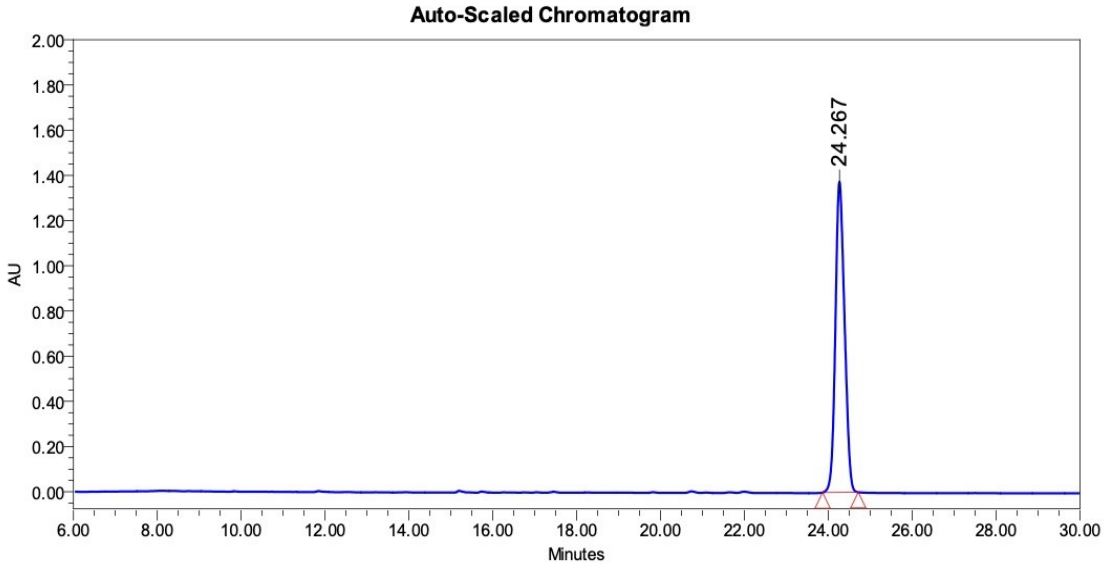


Figure S6: High-performance liquid chromatogram (HPLC) curves of **TPTZPO** in acetonitrile and water mixture using C18 column and 240 nm UV detector.

SAMPLE INFORMATION

Sample Name:	TPTZPS	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	280322_PT LAB SAMPLES
Vial:	1	Acq. Method Set:	DG
Injection #:	1	Processing Methoc	290322_PT lab
Injection Volume:	80.00 ul	Channel Name:	2998 Ch2 240nm@4.8nm
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	2998 Ch2 240nm@4.8nm
Date Acquired:	3/29/2022 1:46:58 AM IST		
Date Processed:	3/29/2022 3:41:50 AM IST		



Peak Results

	Name	RT	Area	Height	Amount	Units
1		24.267	20782139	1375204		

Figure S7: High-performance liquid chromatogram (HPLC) curves of **TPTZPS** in acetonitrile and water mixture using C18 column and 240 nm UV detector.

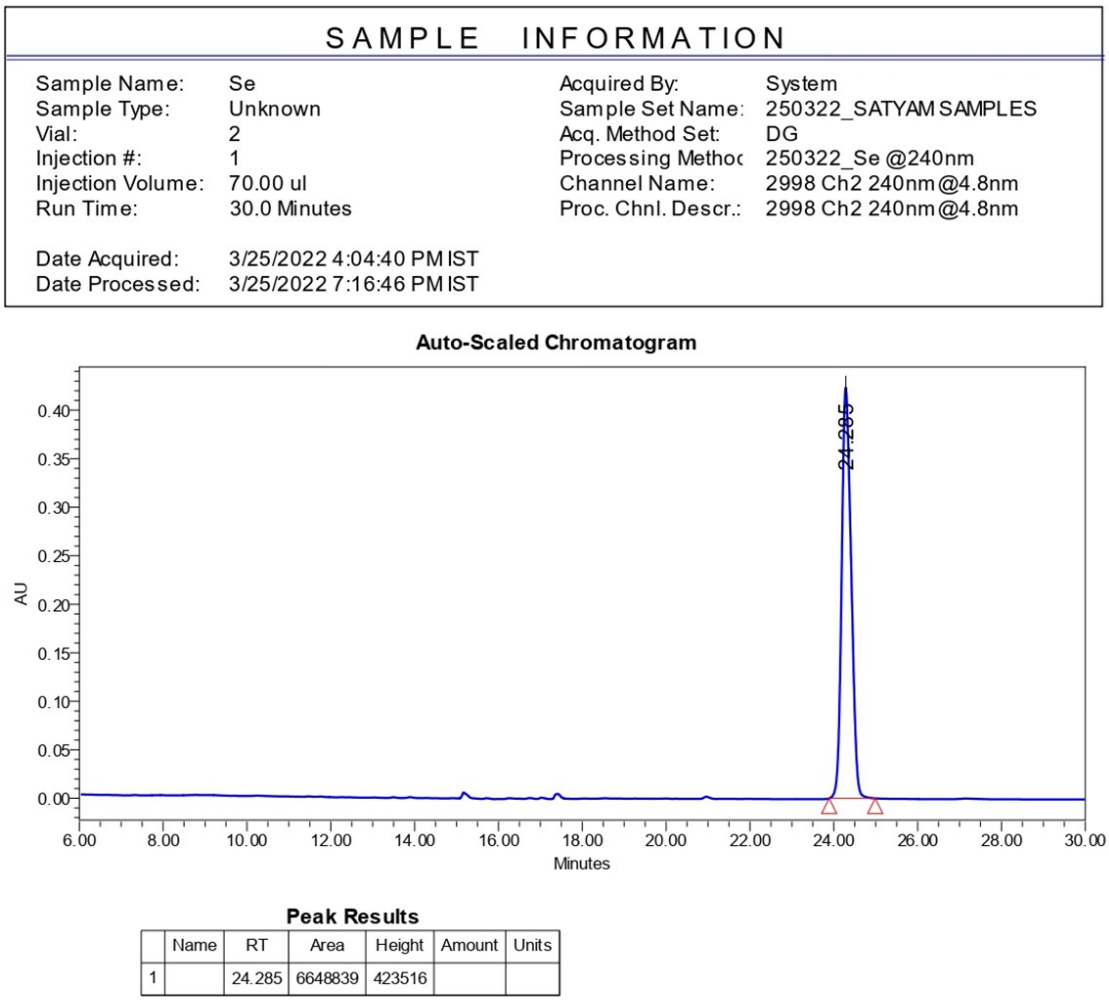


Figure S8: High-performance liquid chromatogram (HPLC) curves of **TPTZPSe** in acetonitrile and water mixture using C18 column and 240 nm UV detector.

Table S1. Crystallographic data and refinement parameters

Compound	**TPTZPO**	**TPTZPS**	**TPTZPSe**
Empirical formula	$C_{36}H_{24}N_3OPS_3$	$C_{36}H_{24}N_3PS_4$	$C_{36}H_{24}N_3PS_3Se$
FW	641.73	657.790	704.72
T (K)	293(2) K	293(2) K	293(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C 2/c	P 2_1	P 2_1
a/Å	27.1703(13)	9.351(4)	9.3508(4)
b/Å	14.9942(8)	14.475(6)	14.3508(7)
c/Å	17.8873(9)	12.042(5)	11.9256(6)
α/deg	90	90	90
β/deg	111.2030(10)	111.149(9)	111.3960(10)
γ/deg	90	90	90
V/Å^3	6793.9(6)	1520.1(11)	1490.02(12)
Z	8	2	2
ρ_{calcd} (gcm^{-3})	1.255	1.437	1.573
μ (Mo Kα) (mm^{-1})	0.297	0.398	1.574
λ/Å	0.71073	0.71073	0.71073
F (000)	2656	680	680
Collected reflns	100810	29912	48856
Unique reflns	7860	2938	6851
GOF (F2)	0.705	1.098	0.927
R1 [I>2σ(I)][a]	0.0535	0.0210	0.0264
wR2 [I>2σ(I)][b]	0.2186	0.0454	0.0562
CCDC Number	1977279	1916761	1916789

[a] $R1 = \Sigma \big| |Fo| - |Fc| \big| / \Sigma |Fo|$. [b] $wR2 = [\Sigma\{w(Fo^2 - Fc^2)^2\}/\Sigma\{w(Fo^2)$

Table S2. Bond lengths and phenothiazine puckering angles measured from crystal structure

Compound	P=X (Å)	P-N Bond lengths (Å)	Phenothiazine puckering angle
TPTZPO	1.462 (3)	P1-N1 1.683(3)	P1-N1-S1 (131.55°)
		P1-N2 1.663(4)	P1-N1-S1 (126.97°)
		P1-N3 1.682(3)	P1-N1-S1 (141.29°)
TPTZPS	1.924 (2)	P1-N1 1.687(3)	P1-N1-S1 (131.59°)
		P1-N2 1.675(4)	P1-N1-S1 (128.00°)
		P1-N3 1.689(3)	P1-N1-S1 (132.71°)
TPTZPSe	2.086 (1)	P1-N1 1.687(3)	P1-N1-S1 (132.57°)
		P1-N2 1.688(3)	P1-N1-S1 (128.38°)
		P1-N3 1.682(3)	P1-N1-S1 (131.50°)

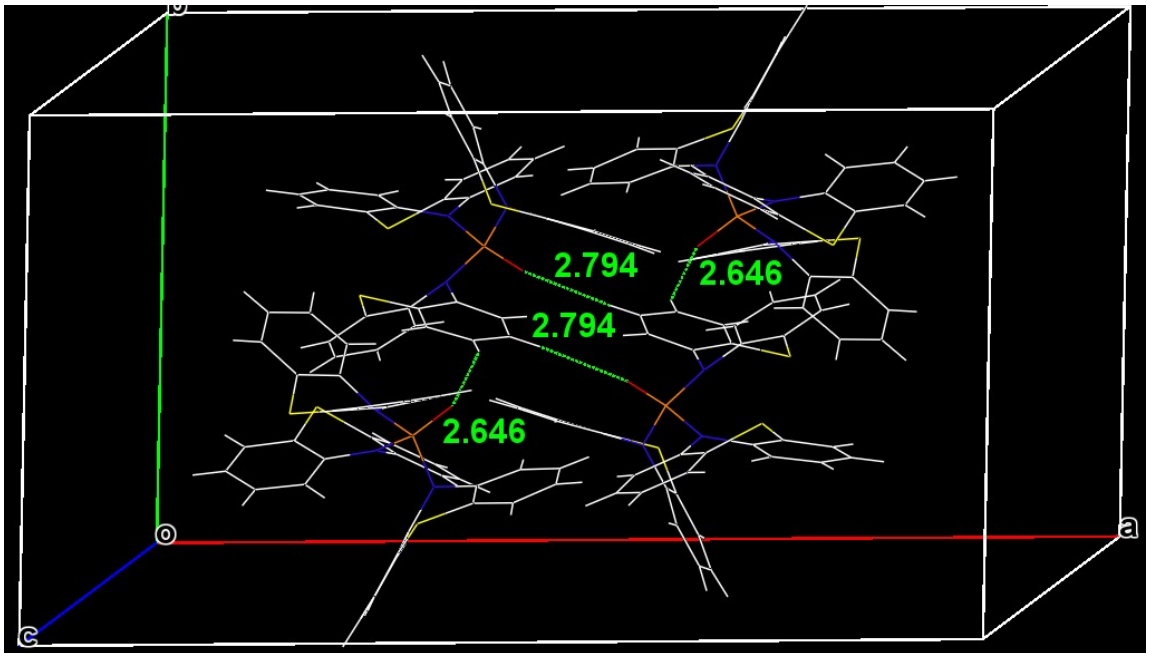


Figure S9: P=O…….H-C intermolecular interactions observed in **TPTZPO**.

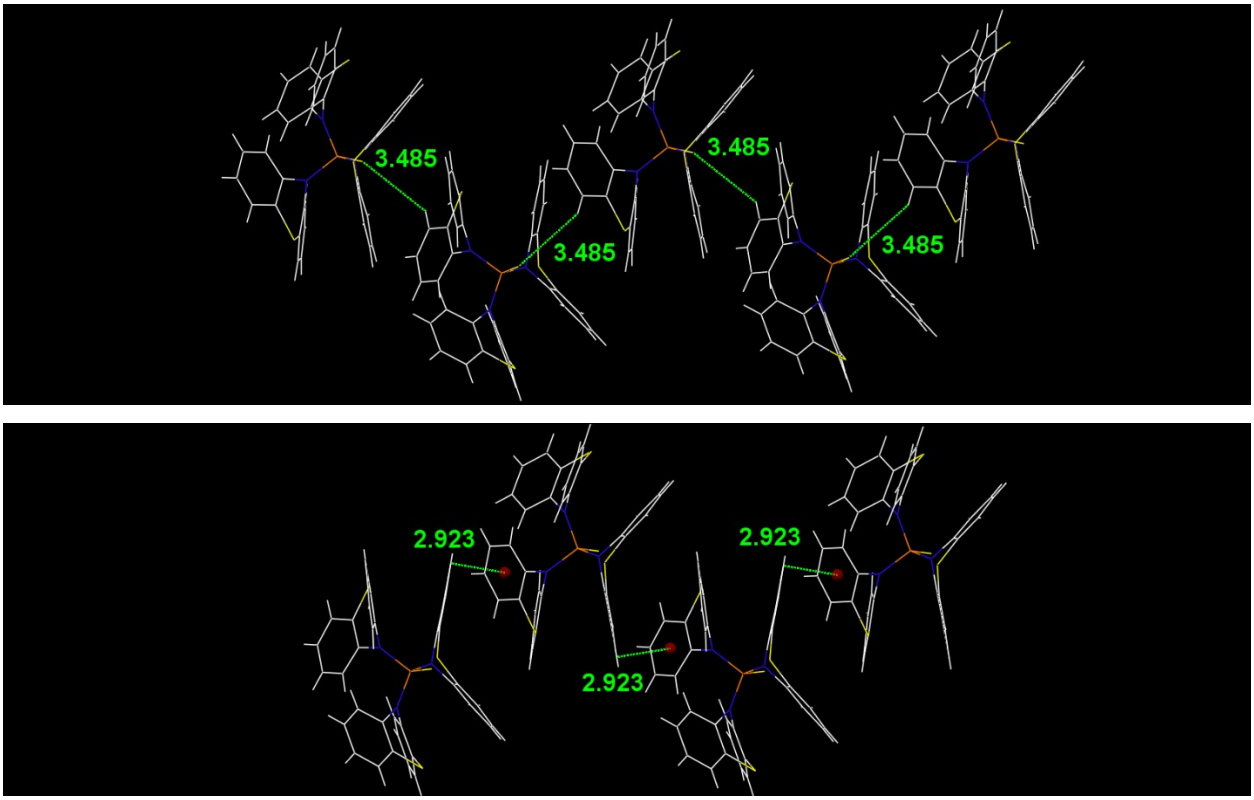


Figure S10: Intermolecular interaction diagram of compound **TPTZPS**.

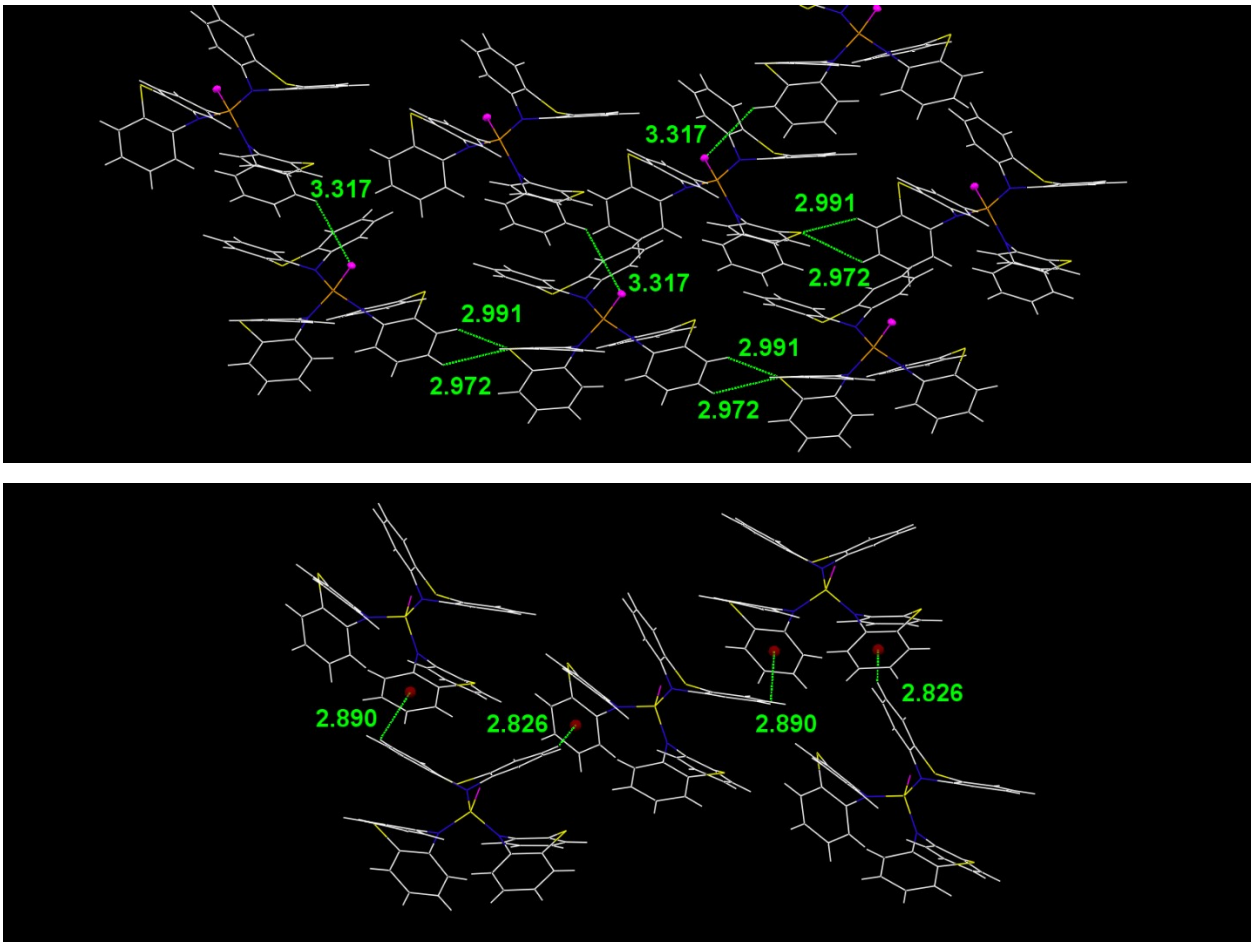


Figure S11: Intermolecular interaction diagram of compound **TPTZPSe**.

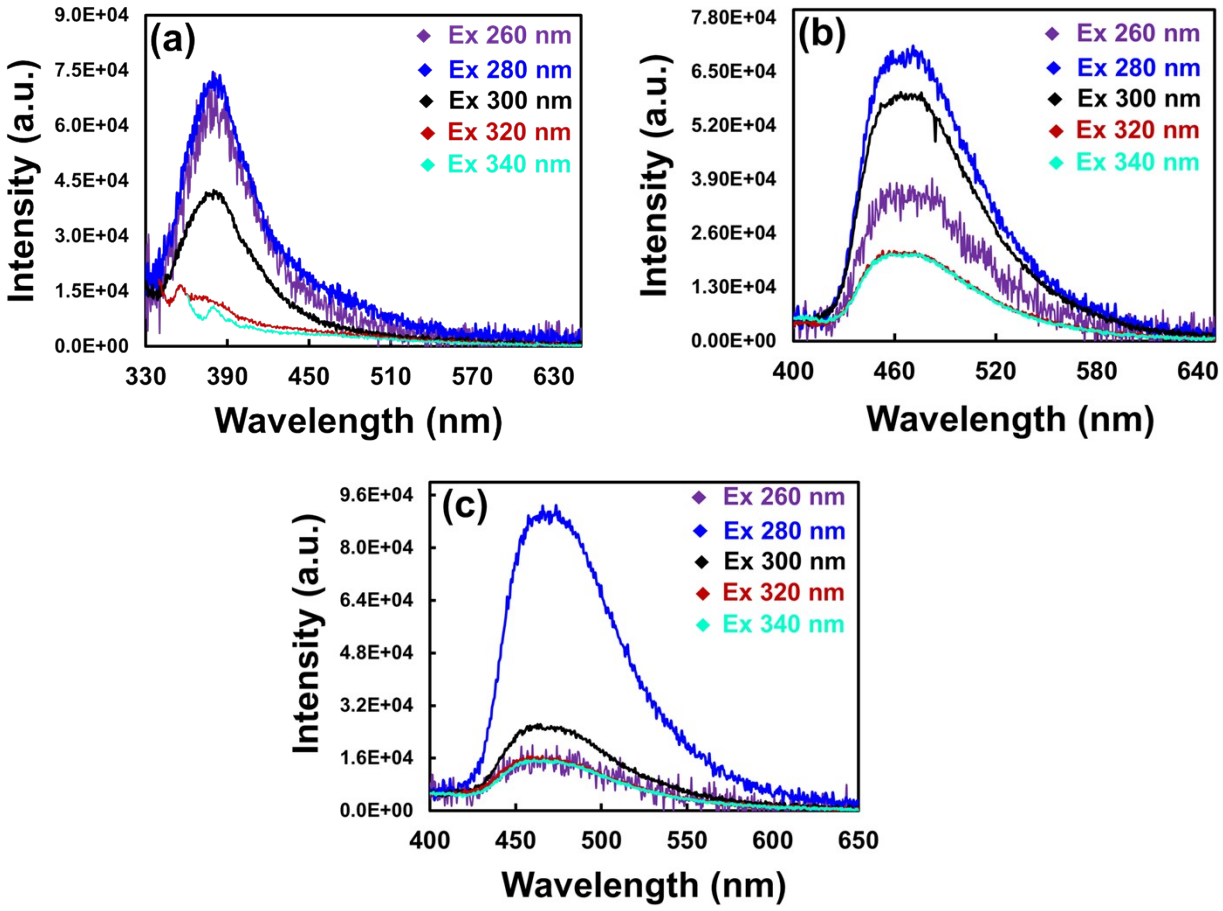


Figure S12: Excitation wavelength dependent fluorescence spectra of compound **TPTZPO** (a), **TPTZPS** (b) and **TPTZPSe** (c) in dichloromethane (conc. 10^{-4} M). No change in the emission maxima and spectral shape clearly indicate the emission from single species not from aggregates or impurities.

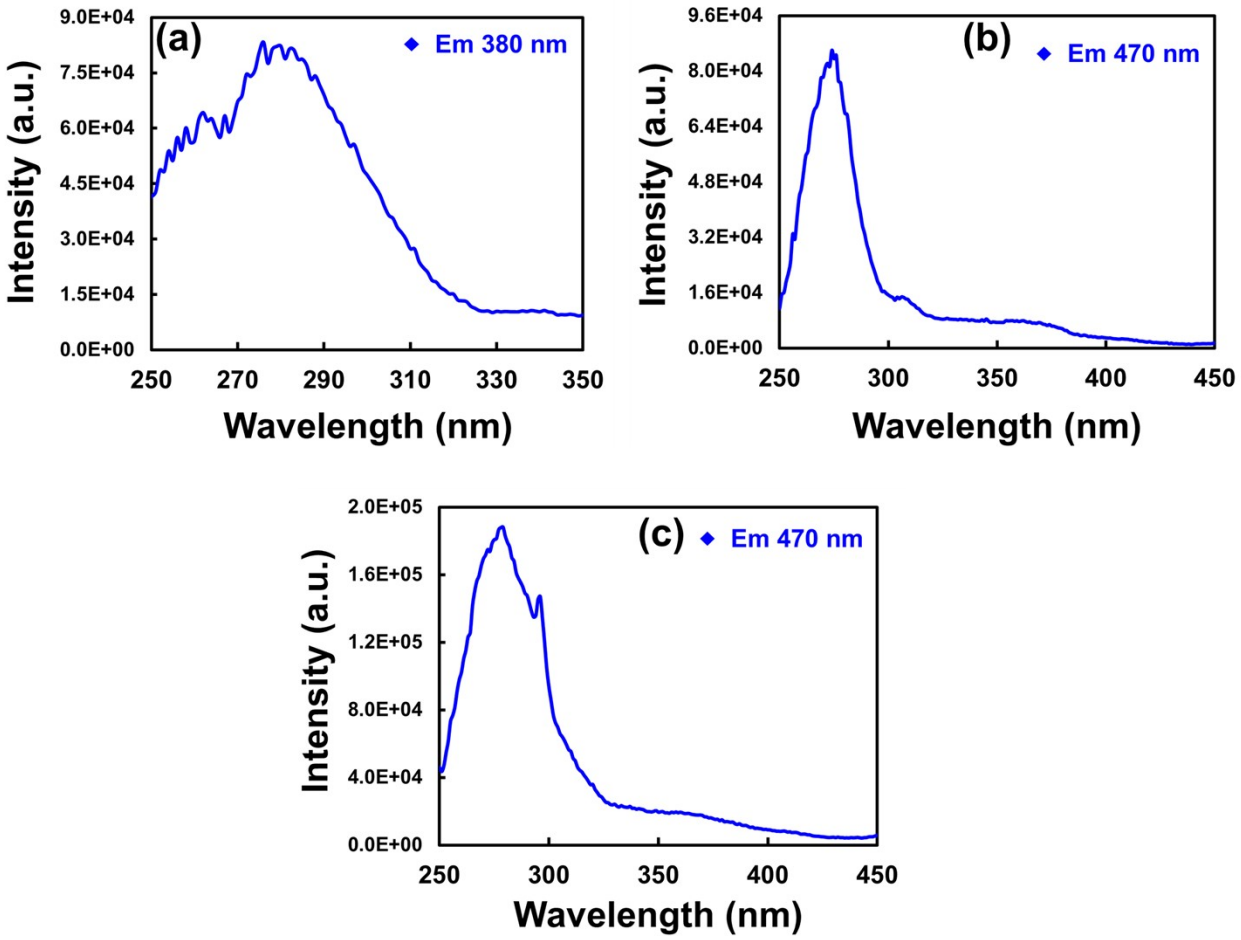


Figure S13: Excitation spectra of compound **TPTZPO** (a), **TPTZPS** (b) and **TPTZPSe** (c) in dichloromethane (conc. 10^{-4} M). Excitation spectra reproduced the absorption spectra of corresponding compounds clearly indicate the emission from single species not from aggregates or impurities.

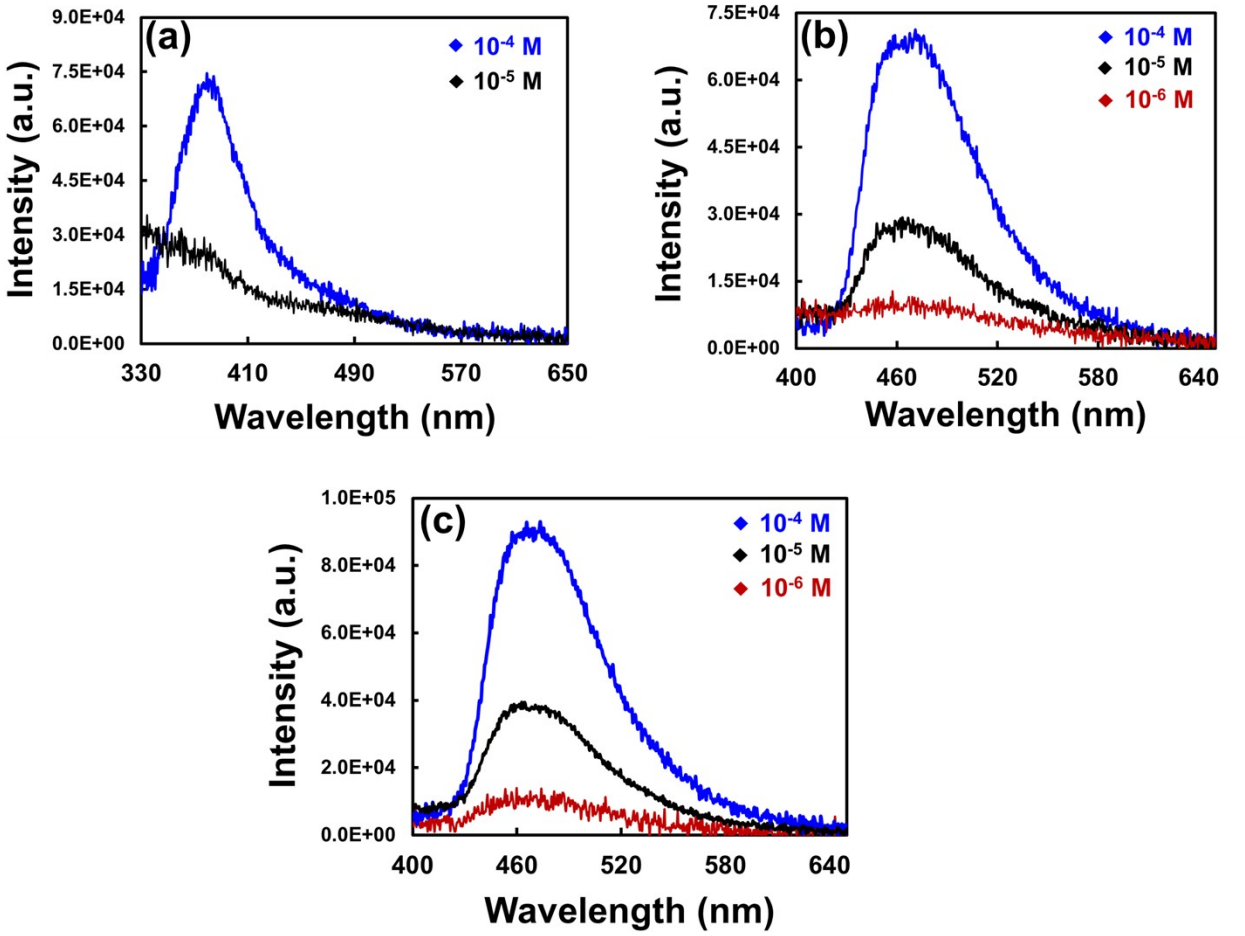


Figure S14: Concentration dependent PL spectra of compound **TPTZPO** (a), **TPTZPS** (b) and **TPTZPSe** (c) in dichloromethane(λ_{ex} = 280 nm).

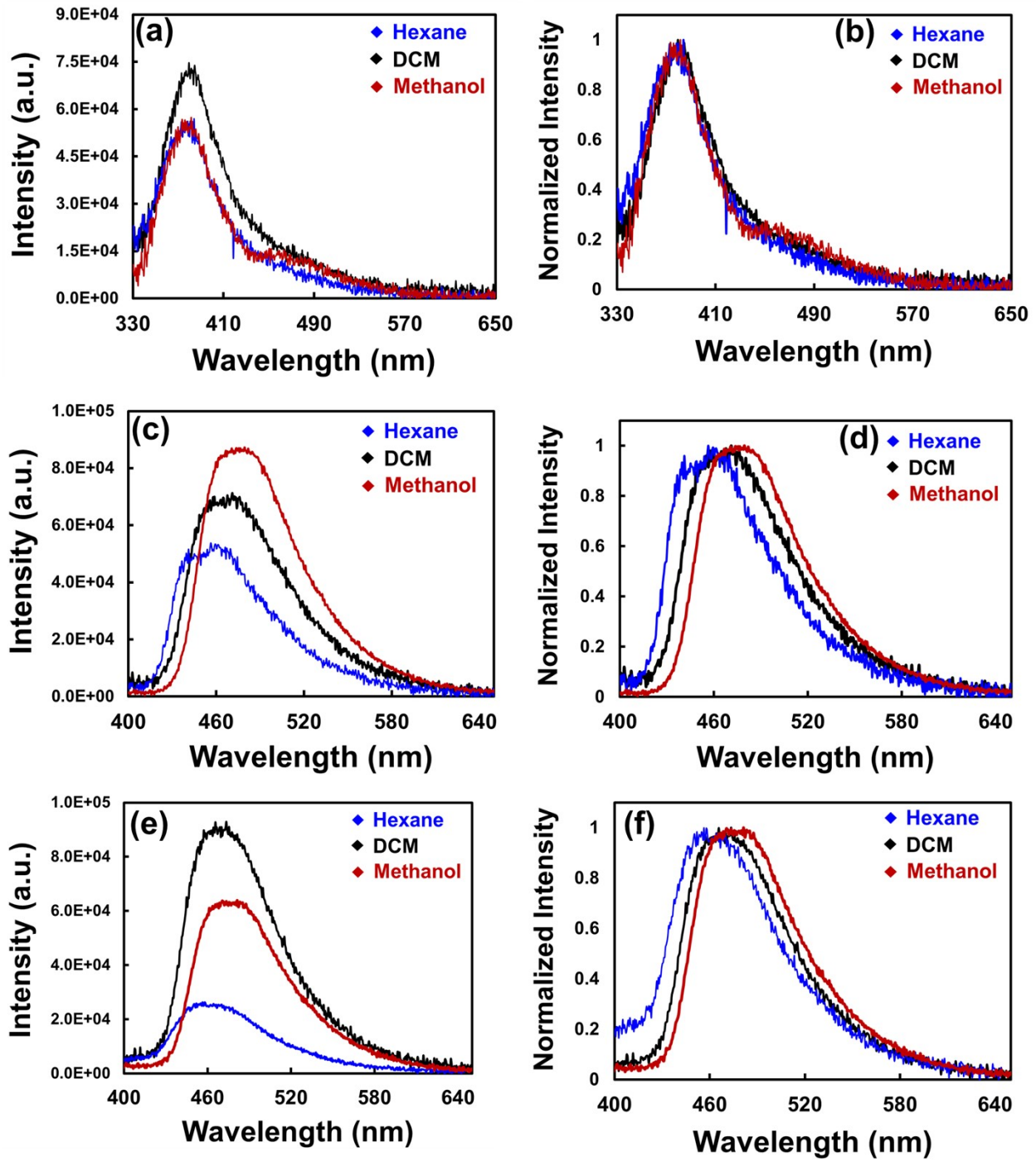


Figure S15: Fluorescence spectra and corresponding normalized spectra of **TPTZPO** (a, b), **TPTZPS** (c, d) and **TPTZPSe** (e, f) in different solvents (λ_{ex} = 280 nm).

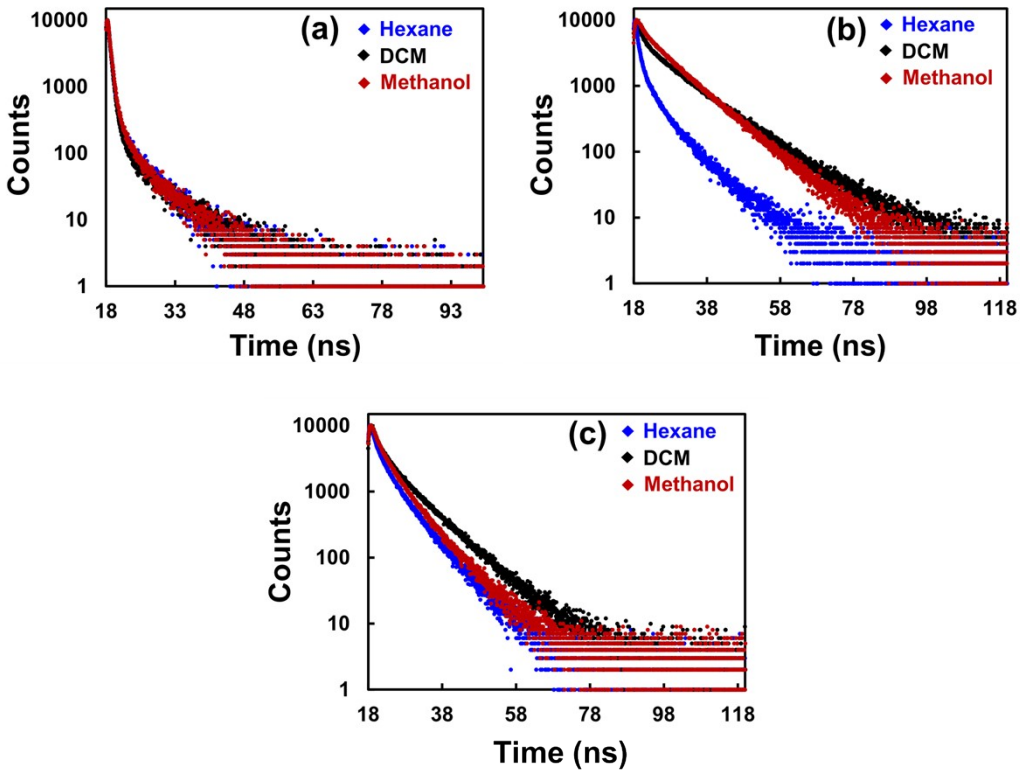


Figure S16: Fluorescence decay profile of **TPTZPO** (a), **TPTZPS** (b) and **TPTZPSe** (c) in different solvents (conc. 10^{-4} M and λ_{ex} = 296 nm).

Table S3. Fluorescence lifetime of **TPTZPO, TPTZPS** and **TPTZPSe** in different solvents (conc 10^{-4} M)

Compound	Fl lifetime in solutions (ns)	
TPTZPO	Hexane (λ_{em} = 380 nm)	τ = 1.50 ns
	DCM (λ_{em} = 380 nm)	τ = 1.32 ns
	Methanol (λ_{em} = 380 nm)	τ = 1.46 ns
TPTZPS	Hexane (λ_{em} = 456 nm)	τ = 1.50 ns
	DCM (λ_{em} = 471 nm)	τ = 8.32 ns
	Methanol (λ_{em} = 479 nm)	τ = 7.06 ns
TPTZPSe	Hexane (λ_{em} = 458 nm)	τ = 1.65 ns
	DCM (λ_{em} = 465 nm)	τ = 6.44 ns
	Methanol (λ_{em} = 481 nm)	τ = 2.18 ns

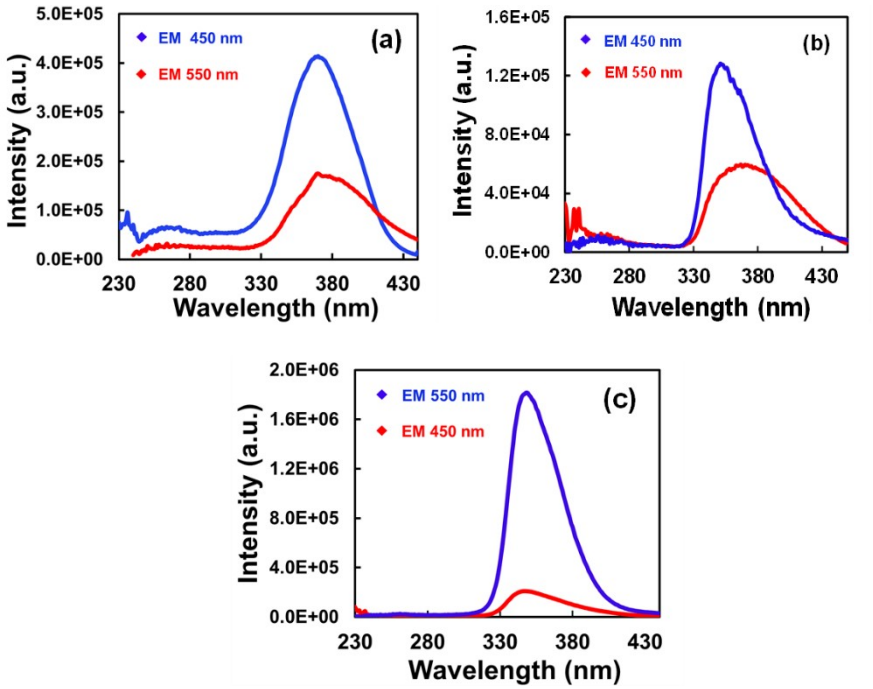


Figure S17: Emission wavelength dependent excitation spectra of crystals of **TPTZPO** (a), **TPTZPS** (b) and **TPTZPSe**(c).

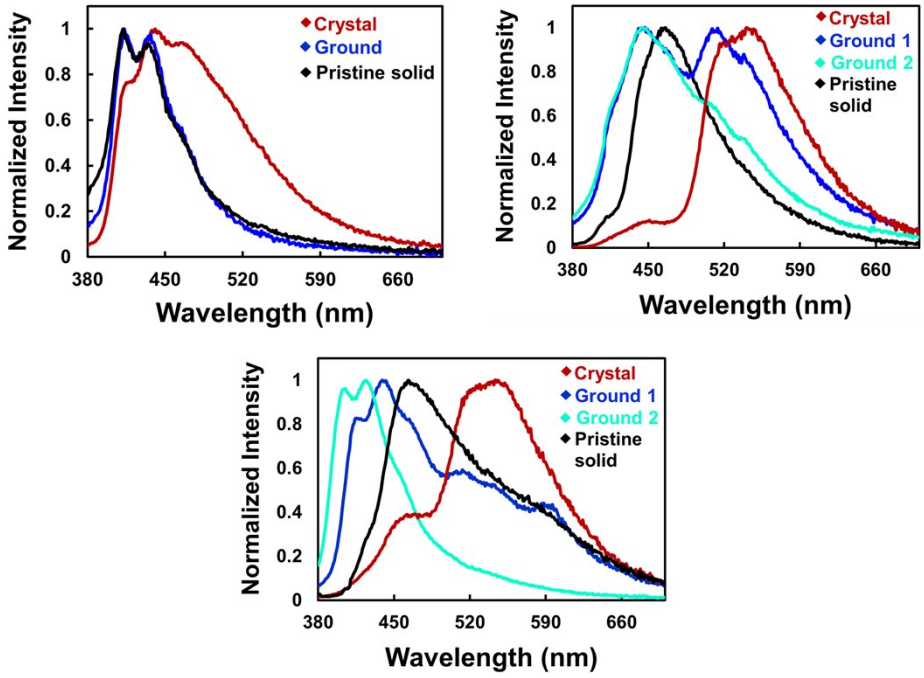


Figure S18: Normalized photoluminescence spectra of crystals, ground samples, and pristine samples of **TPTZPO** (a), **TPTZPS** (b), and **TPTZPSe** (c) (λ_{ex} = 360 nm). (Ground 1 indicates grinding with a mortar and pestle for 5 minutes, and ground 2 indicates heavily grinding for 15 minutes).

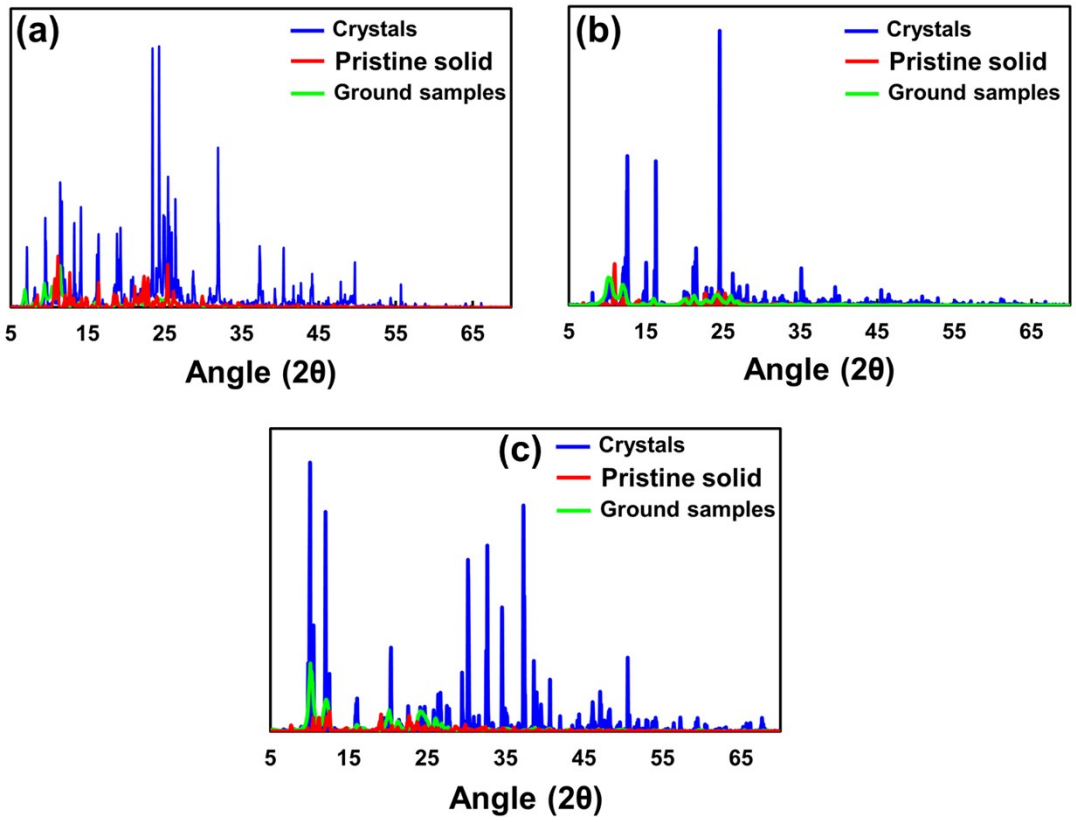


Figure S19: Powder XRD pattern of crystals, pristine solids, and ground samples of **TPTZPO** (a), **TPTZPS** (b), and **TPTZPSe** (c).

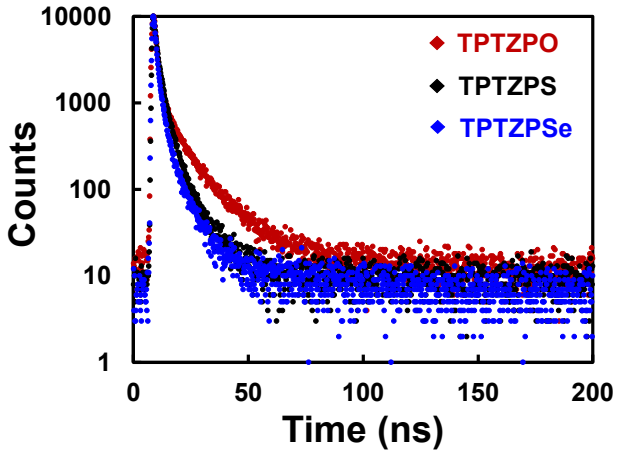


Figure S20: Fluorescence decay profile of crystals of **TPTZPO**, **TPTZPS** and **TPTZPSe** (λ_{em} = 450 nm).

Table S4. Fluorescence lifetime data of crystals of **TPTZPO** (a), **TPTZPS** (b), and **TPTZPSe**, λ_{ex} = 375 nm, λ_{em} = 450 nm.

Compound	Fluorescence Lifetime
TPTZPO	τ_1 = 1.58 ns (40.36 %), τ_2 = 11.37 ns (59.64 %)
TPTZPS	τ_1 = 2.10 ns (61.21 %), τ_2 = 7.09 ns (38.79 %)
TPTZPSe	τ_1 = 1.48 ns (59.77 %), τ_2 = 6.74 ns (40.23 %)

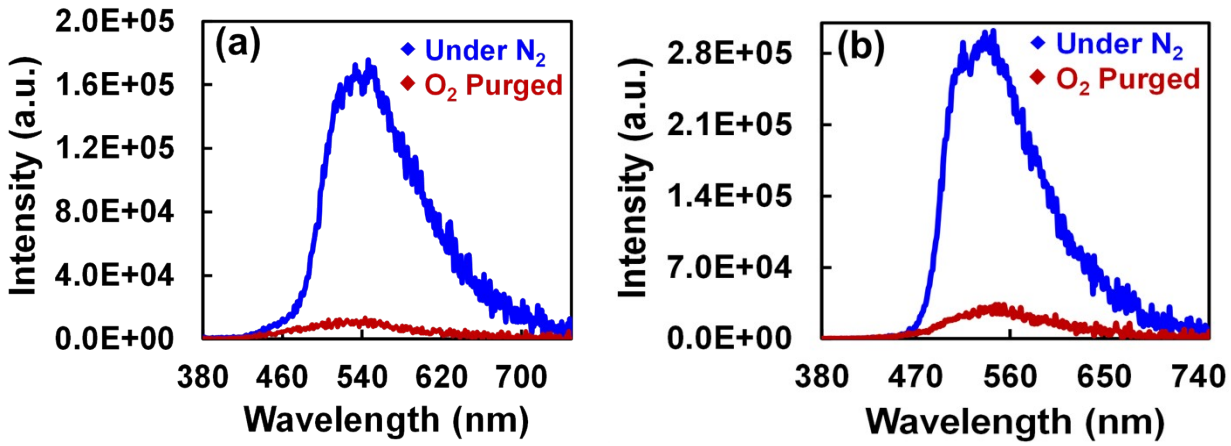


Figure S21: Phosphorescence spectra of a thin-film of **TPTZPO** (a), and **TPTZPSe** (b) under N_2 and O_2 atmosphere (30 µs delay using microsecond flash lamp, λ_{ex} = 360 nm).

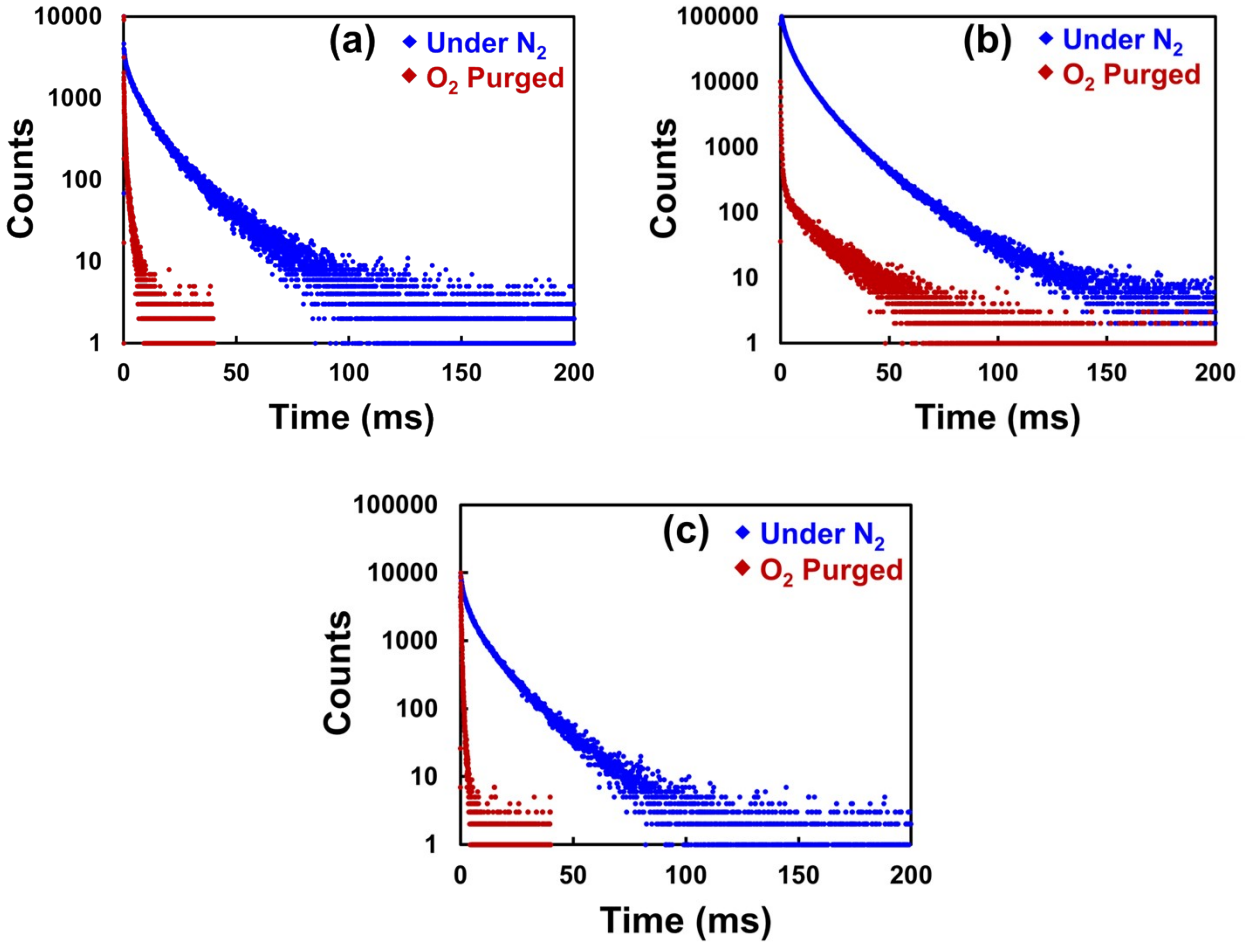


Figure S22: Phosphorescence lifetime decay profile of thin film of **TPTZPO**, λ_{em} = 540 nm (a), **TPTZPS**, λ_{em} = 540 nm (b), and **TPTZPSe**, λ_{em} = 543 nm (c) under N_2 and O_2 with 30 µs delay, λ_{ex} = 360 nm.

Table S5. Phosphorescence lifetime data of thin film of **TPTZPO**, λ_{em} = 540 nm (a), **TPTZPS**, λ_{em} = 540 nm (b), and **TPTZPSe**, λ_{em} = 543 nm (c) under N_2 and O_2 with 30 µs delay, λ_{ex} = 360 nm.

Compound	N_2	O_2
TPTZPO	τ_1 = 3.58 ms (28.74 %) τ_2 = 13.28 ms (71.26 %)	τ_1 = 256.09 µs (39.80 %) τ_2 = 1.53 ms (60.20 %)
TPTZPS	τ_1 = 1.99 ms (16.65 %) τ_2 = 16.89 ms (83.35 %)	τ_1 = 436.62 µs (24.55 %) τ_2 = 10.20 ms (75.45 %)
TPTZPSe	τ_1 = 3.12 ms (31.76 %) τ_2 = 12.08 ms (68.24 %)	τ_1 = 205.23 µs (59.39 %) τ_2 = 621.7 µs (40.61 %)

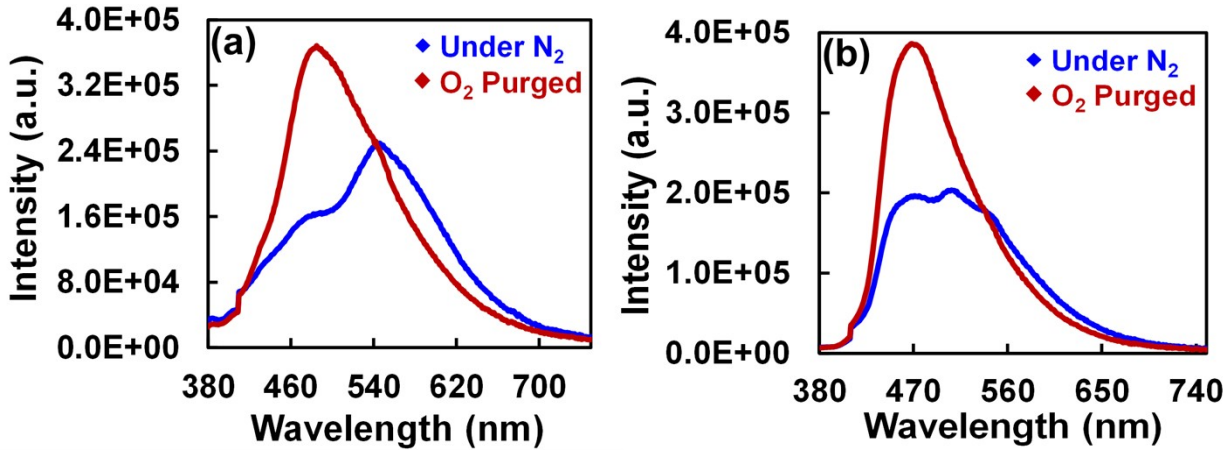


Figure S23: Prompt spectra of thin film of **TPTZPO** (a), **TPTZPSe** (b) under N_2 and O_2 atmosphere (λ_{ex} = 360 nm).

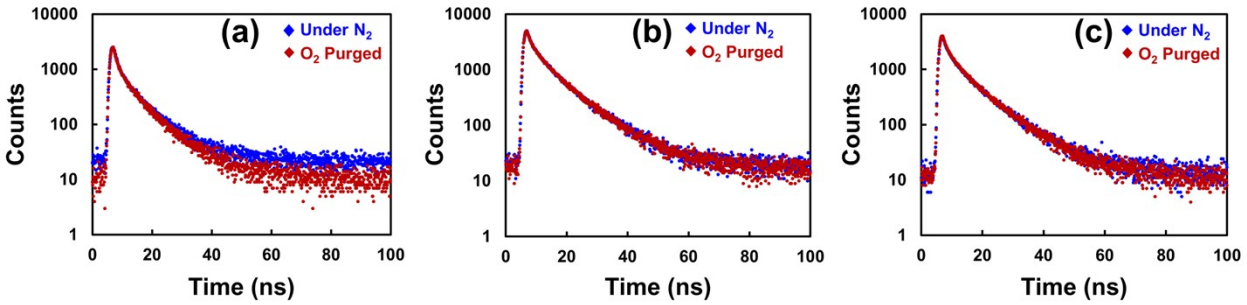


Figure S24: Fluorescence lifetime decay profile of thin film of **TPTZPO** (a), **TPTZPS** (b), and **TPTZPSe** (c) under N_2 and O_2 atmosphere (λ_{ex} = 375 nm, λ_{em} = 470 nm).

Table S6. Fluorescence lifetime data of thin film of **TPTZPO** (a), **TPTZPS** (b), and **TPTZPSe** (c) under N_2 and O_2, λ_{ex} = 375 nm, λ_{em} = 470 nm.

Compound	N_2	O_2
TPTZPO	τ_1 = 1.53 ns (26.66 %) τ_2 = 8.17 ns (73.34 %)	τ_1 = 1.58 ns (39.80 %) τ_2 = 8.04 ns (60.20 %)
TPTZPS	τ_1 = 2.13 ns (22.71 %) τ_2 = 9.43 ns (77.29 %)	τ_1 = 2.11 ns (21.89 %) τ_2 = 9.42 ns (78.11 %)
TPTZPSe	τ_1 = 2.07 ns (24.93 %) τ_2 = 9.42 ns (75.07 %)	τ_1 = 2.02 ns (23.76 %) τ_2 = 9.41 ns (76.24 %)

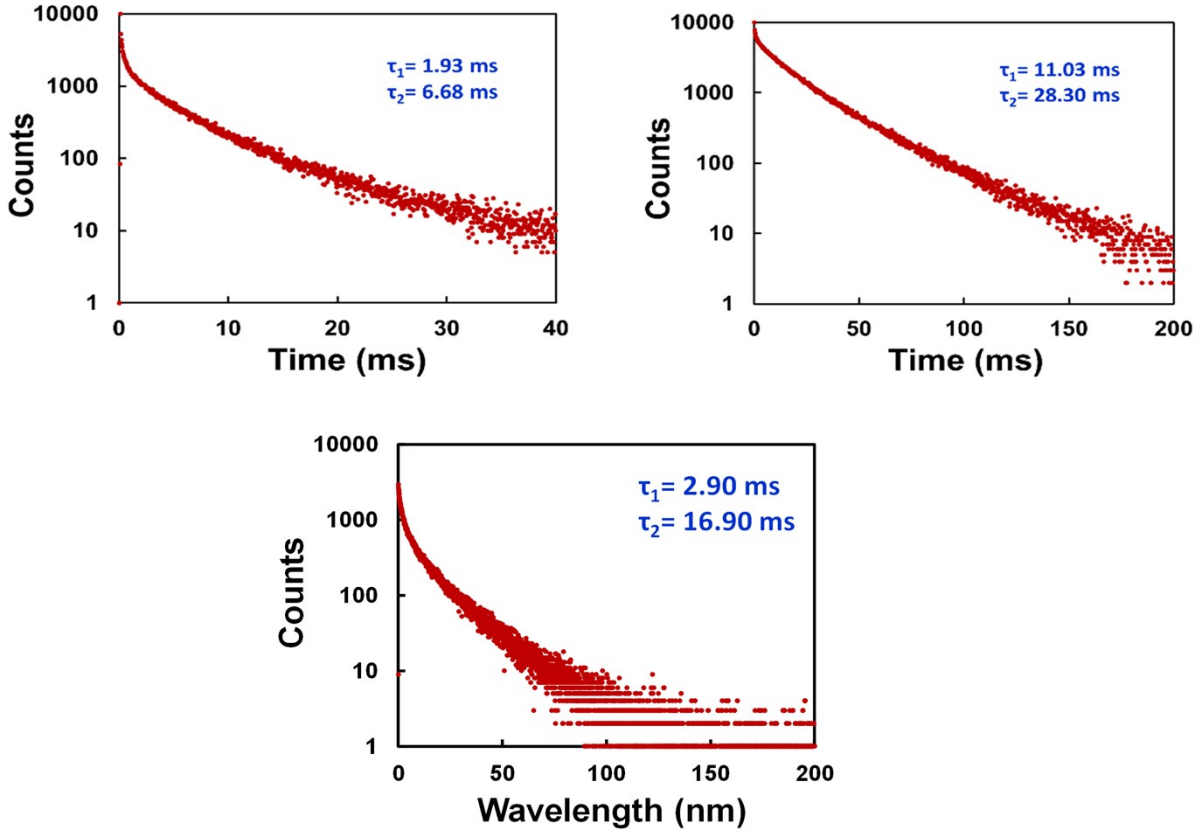


Figure S25: Phosphorescence decay profile of pristine solids of **TPTZPO** (upper left), **TPTZPS** (upper right) and **TPTZPSe** (down) (λ_{em} = 550 nm).

Table S7. Triplet excited state lifetime of crystals of **TPTZPO**, **TPTZPS** and **TPTZPSe** at different temperatures.

Compound	Temperature	Lifetime	
		τ_1 (ms)	τ_2 (ms)
TPTZPO	77 K	21.27 (15.71 %)	61.03 (84.29 %)
	140 K	16.32 (12.95 %)	53.45 (87.05 %)
	200K	16.00 (14.82 %)	43.81 (85.18 %)
	240 K	11.62 (21.99 %)	31.55 (78.01 %)
	298 K	1.42 (16.39 %)	10.28 (83.61 %)
TPTZPS	77 K	12.86 (14.58 %)	53.33 (85.42 %)
	140 K	20.42 (17.16 %)	50.54 (82.84 %)
	200K	19.79 (18.29 %)	46.31 (81.71 %)
	240 K	12.73 (7.68 %)	36.68 (92.32 %)
	298 K	10.43 (9.56 %)	28.78 (90.44 %)
TPTZPSe	77 K	6.79 (4.29 %)	58.38 (95.71 %)
	140 K	12.45 (3.92 %)	53.18 (96.08 %)
	200K	11.70 (2.51 %)	44.87 (97.49 %)
	240 K	9.01 (1.96 %)	38.89 (98.04 %)
	298 K	6.0 (29.83 %)	17.0 (70.17 %)

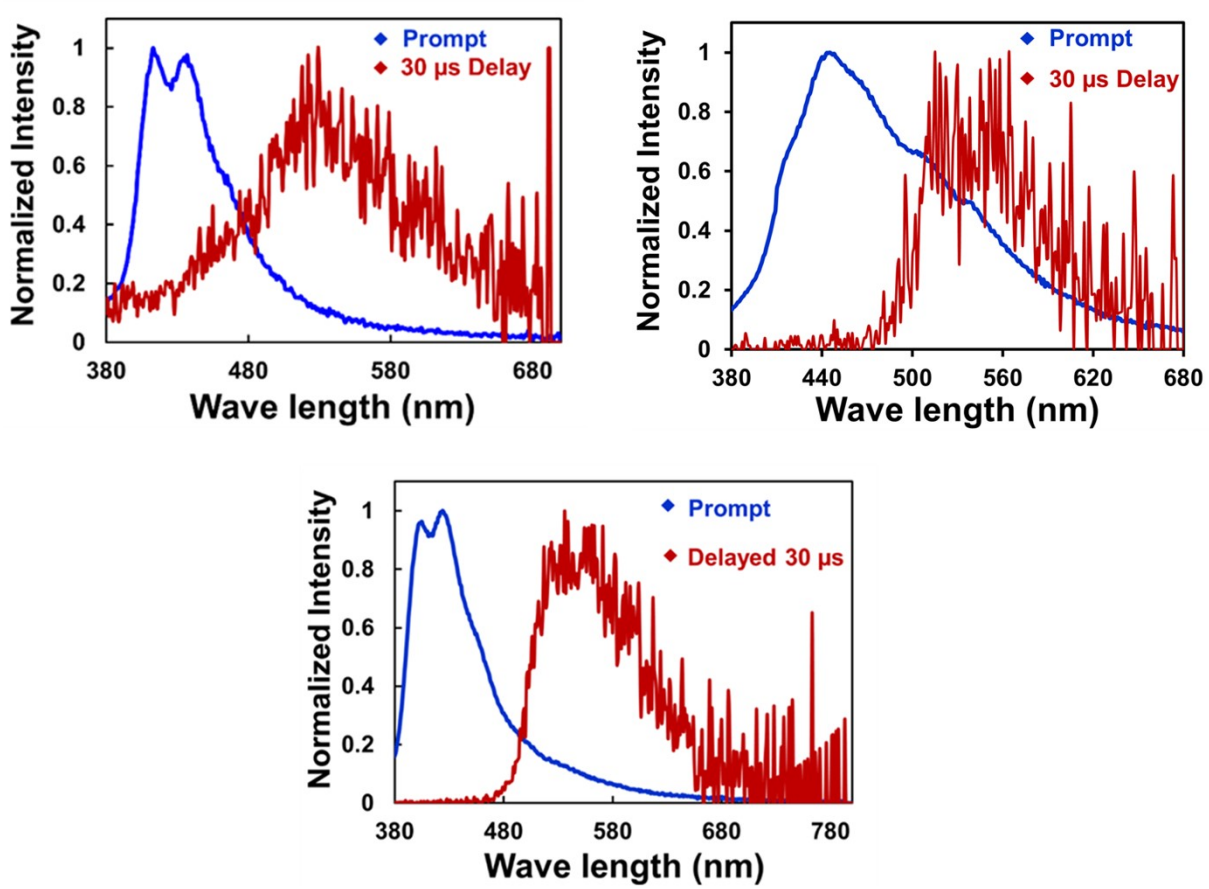


Figure S26: Prompt (blue line) and phosphorescence (red line) spectra of **TPTZPO** (upper left), **TPTZPS** (upper right), **TPTZPSe** (bottom) after grinding.

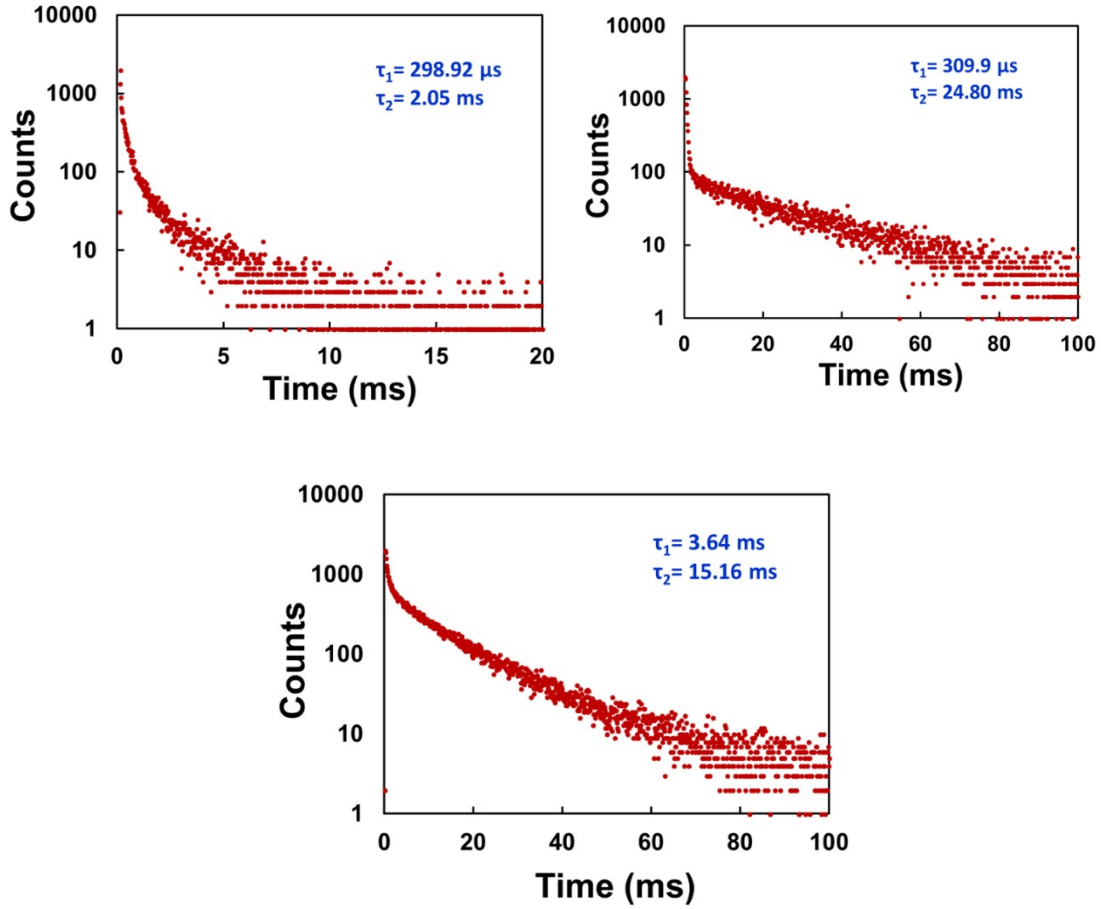


Figure S27: Phosphorescence decay profile of ground samples of **TPTZPO** (upper left), **TPTZPS** (upper right), **TPTZPSe** (down) (λ_{em}= 550 nm)

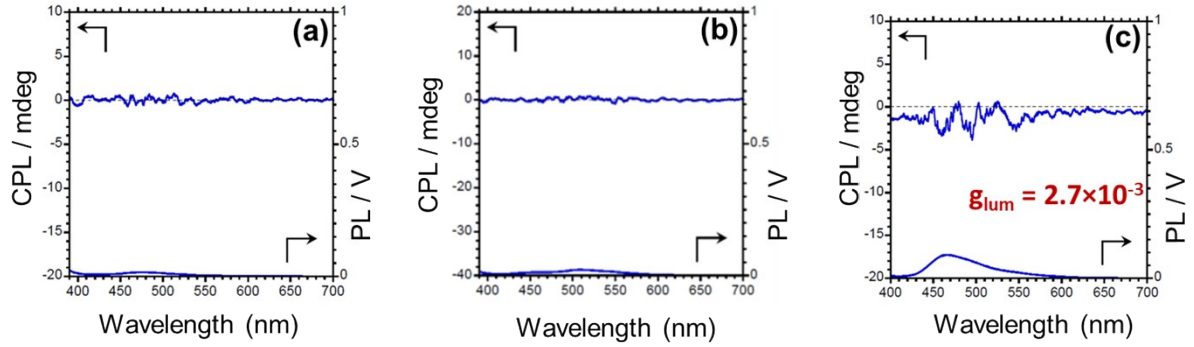


Figure S28: Circularly polarized luminescence (CPL) spectra and corresponding photoluminescence spectra of ground samples (ground from crystals) of **TPTZPO** (a), **TPTZPS** (b), and **TPTZPSe** (c), λ_{ex} = 360 nm (g_{CPL} = 2.7 x 10^{-3} (**TPTZPSe**)) (CPL spectra-Top, Photoluminescence spectra-Bottom).

Table S8. DFT optimized geometry parameters of **TPTZPO** in ground and excited states.

Compound		PTZ-1 (Light Blue)	PTZ-2 (Light Green)	PTZ-3 (Purple)
Ground state (S_0)	N-P (Å)	1.680	1.702	1.693
	N-C (Å)	1.429, 1.434	1.434, 1.439	1.439, 1.432
	S-C (Å)	1.772, 1.773	1.766, 1.772	1.764, 1.764
	C-C (Å)	1.397, 1.395, 1.389, 1.388, 1.388, 1.388, 1.388, 1.387, 1.388, 1.387, 1.388, 1.386	1.395, 1.397, 1.388, 1.385, 1.389, 1.385, 1.390, 1.389, 1.387, 1.387, 1.386, 1.389	1.349, 1.394, 1.390, 1.385, 1.397, 1.384, 1.390, 1.389, 1.387, 1.385, 1.385, 1.389
	Puckering angle	124.95°	131.43°	140.07°
Singlet state (S_1)	N-P (Å)	1.707	1.734	1.721
	N-C (Å)	1.429, 1.430	1.431, 1.437	1.404, 1.408
	S-C (Å)	1.770, 1.772	1.769, 1.772	1.697, 1.706
	C-C (Å)	1.397, 1.393, 1.390, 1.388, 1.388, 1.388, 1.387, 1.389, 1.389, 1.388, 1.386, 1.389	1.395, 1.396, 1.388, 1.386, 1.389, 1.386, 1.390, 1.389, 1.388, 1.388, 1.387, 1.388	1.443, 1.449, 1.413, 1.366, 1.421, 1.363, 1.412, 1.404, 1.370, 1.421, 1.362, 1.415
	Puckering angle	130.17°	128.16°	159.7°
Triplet state (T_1)	N-P (Å)	1.707	1.734	1.720
	N-C (Å)	1.430, 1.428	1.432, 1.437	1.434, 1.410
	S-C (Å)	1.771, 1.772	1.769, 1.772	1.755, 1.730
	C-C (Å)	1.394, 1.396, 1.389, 1.388, 1.387, 1.387, 1.387, 1.39, 1.388, 1.387, 1.387, 1.388	1.395, 1.394, 1.388, 1.387, 1.388, 1.387, 1.388, 1.388, 1.386, 1.389, 1.386, 1.390	1.490, 1.400, 1.397, 1.381, 1.390, 1.380, 1.392, 1.378, 1.392, 1.449, 1.341, 1.458
	Puckering angle	130.02°	132.27°	143.43°

(PTZ-1: Phenothiazine-1, PTZ-2: Phenothiazine-2, PTZ-3: Phenothiazine-3)

Table S9. DFT optimized geometry parameters of **TPTZPS** in ground and excited states

Compound		PTZ-1 (Light Blue)	PTZ-2 (Light Green)	PTZ-3 (Purple)
Ground state (S_0)	N-P (Å)	1.703	1.723	1.707
	N-C (Å)	1.435, 1.441	1.429, 1.437	1.439, 1.444
	S-C (Å)	1.766, 1.767	1.766, 1.768	1.767, 1.770
	C-C (Å)	1.392, 1.398, 1.392, 1.388, 1.387, 1.388, 1.388, 1.391, 1.386, 1.388, 1.384, 1.390	1.395, 1.397, 1.390, 1.388, 1.388, 1.387, 1.388, 1.389, 1.387, 1.387, 1.387, 1.390	1.394, 1.397, 1.385, 1.387, 1.387, 1.387, 1.387, 1.388, 1.386, 1.388, 1.386, 1.389
	Puckering angle	130.23°	133.82°	125.49°
Singlet state (S_1)	N-P (Å)	1.737	1.757	1.742
	N-C (Å)	1.428, 1.431	1.420, 1.424	1.427, 1.428
	S-C (Å)	1.769, 1.770	1.770, 1.771	1.765, 1.770
	C-C (Å)	1.395, 1.398, 1.389, 1.388, 1.388, 1.387, 1.388, 1.393, 1.387, 1.387, 1.388, 1.387	1.395, 1.398, 1.391, 1.389, 1.387, 1.387, 1.388, 1.391, 1.387, 1.387, 1.387, 1.388	1.397, 1.399, 1.388, 1.388, 1.386, 1.387, 1.388, 1.3892, 1.388, 1.387, 1.390, 1.386
	Puckering angle	132.92°	133.70°	137.72°
Triplet state (T_1)	N-P (Å)	1.737	1.757	1.742
	N-C (Å)	1.426, 1.430	1.422, 1.420	1.425, 1.428
	S-C (Å)	1.770, 1.769	1.770, 1.771	1.764, 1.770
	C-C (Å)	1.397, 1.395, 1.393, 1.388, 1.387, 1.388, 1.387, 1.389, 1.388, 1.388, 1.387, 1.389	1.395, 1.398, 1.391, 1.387, 1.387, 1.386, 1.388, 1.391, 1.387, 1.388, 1.386, 1.388	1.400, 1.397, 1.387, 1.394, 1.387, 1.39, 1.386, 1.388, 1.387, 1.387, 1.386, 1.388
	Puckering angle	133.25°	134.08°	137.36°

(PTZ-1: Phenothiazine-1, PTZ-2: Phenothiazine-2, PTZ-3: Phenothiazine-3)

Table S10. DFT optimized geometry parameters of **TPTZPSe** in ground and excited states

Compound		PTZ-1 (Light Blue)	PTZ-2 (Light Green)	PTZ-3 (Purple)
Ground state (S_0)	N-P (Å)	1.702	1.709	1.727
	N-C (Å)	1.436, 1.440	1.439, 1.444	1.429, 1.437
	S-C (Å)	1.776, 1.776	1.768, 1.770	1.766, 1.767
	C-C (Å)	1.392, 1.388, 1.392, 1.388, 1.386, 1.386, 1.388, 1.391, 1.386, 1.388, 1.384, 1.390	1.396, 1.394, 1.385, 1.387, 1.387, 1.387, 1.387, 1.388, 1.386, 1.388, 1.386, 1.389	1.396, 1.397, 1.389, 1.387, 1.388, 1.387, 1.390, 1.390, 1.388, 1.386, 1.386, 1.388
	Puckering angle	131.65°	126.16°	134.74°
Singlet state (S_1)	N-P (Å)	1.707	1.721	1.734
	N-C (Å)	1.424, 1.433	1.430, 1.433	1.440, 1.440
	S-C (Å)	1.779, 1.780	1.772, 1.778	1.777, 1.780
	C-C (Å)	1.403, 1.410, 1.401, 1.391, 1.394, 1.393, 1.394, 1.395, 1.393, 1.392, 1.393, 1.393	1.403, 1.404, 1.491, 1.395, 1.390, 1.395, 1.392, 1.396, 1.393, 1.392, 1.392, 1.396	1.404, 1.405, 1.397, 1.391, 1.393, 1.392, 1.395, 1.394, 1.393, 1.393, 1.393, 1.395
	Puckering angle	132.74°	143.03°	134.34°
Triplet state (T_1)	N-P (Å)	1.707	1.721	1.734
	N-C (Å)	1.431, 1.434	1.437, 1.433	1.424, 1.431
	S-C (Å)	1.774, 1.775	1.767, 1.769	1.771, 1.752
	C-C (Å)	1.395, 1.396, 1.388, 1.387, 1.388, 1.386, 1.388, 1.387, 1.388, 1.386, 1.388, 1.386	1.393, 1.398, 1.386, 1.386, 1.387, 1.387, 1.388, 1.386, 1.388, 1.386, 1.387, 1.388	1.475, 1.405, 1.391, 1.386, 1.387, 1.383, 1.393, 1.361, 1.410, 1.429, 1.352, 1.476
	Puckering angle	121.9°	130.61°	118.51°

(PTZ-1: Phenothiazine-1, PTZ-2: Phenothiazine-2, PTZ-3: Phenothiazine-3)

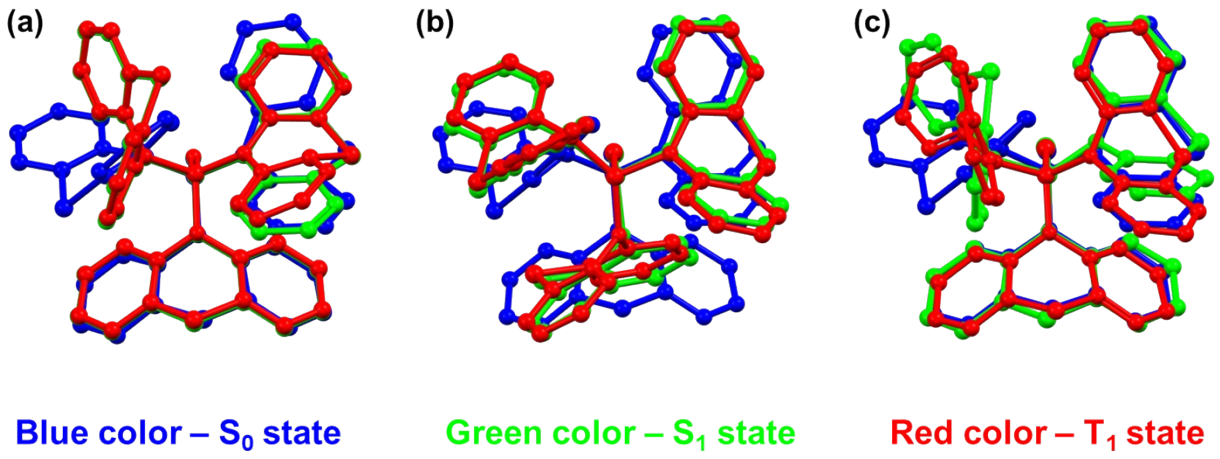


Figure S29: Overlay DFT optimized structure of **TPTZPO** (a), **TPTZPS** (b), and **TPTZPSe** (c) in S_0 (blue color), S_1 (green color), and T_1 (red color) electronic states.

Table S11. Comparison of computational and experimental ΔE_{ST} values of **TPTZPO**, **TPTZPS** and **TPTZPSe.**

Compound	λ_{max}(Prompt)	λ_{max}(Phosphorescence)	ΔE_{ST} Experimental	ΔE_{ST} Theoretical
TPTZPO	441 nm (2.81 eV)	523 nm (2.37 eV)	0.44 eV	0.76 eV
TPTZPS	456 nm (2.71 eV)	542 nm (2.28 eV)	0.43 eV	0.68 eV
TPTZPSe	452 nm (2.74 eV)	536 nm (2.31 eV)	0.43 eV	0.66 eV

Table S12. Computationally calculated energy of excited states and ΔE_{ST} value (in eV) for **TPTZPO**, **TPTZPS** and **TPTZPSe**.

	S_0 - S_1 transition (eV)	n	S_0-T_n transition (eV)	ΔE_{ST} in eV (with respect to S_1)
TPTZPO	4.2271	1	3.4675	0.76
		2	3.5298	0.69
		3	3.5619	0.66
		10	4.1047	0.12
		11	4.1674	0.06
TPTZPS	4.0596	1	3.3764	0.68
		2	3.4372	0.62
		3	3.4445	0.61
		10	4.1100	0.05
		11	4.1531	0.09
TPTZPSe	4.0270	1	3.3614	0.66
		2	3.4414	0.58
		3	3.4442	0.58
		7	3.8611	0.16
		8	3.9082	0.12

Table S13.The matched excited state that contain the same orbital transition components of S_1 of **TPTZPO** revealed by TDDFT calculations. (Triplet state with main ISC channels highlighted with bold letter).

Excited state	n	Energy(eV)	Transition configuration (Percent contribution)
S_n	1	4.2271	**H-1→L+3(3.92), H→L(9.68), H→L+2(4.5), H→L+3(48.02), H→L+5(8.82)**
T_n	1	3.4675	**H-1→L+3(2.88), H→L(5.12), H→L+2(5.13), H→L+3(21.78),H→L+5(3.92)**
	2	3.5298	H-1→L(2.0), H-1→L+2(8.0), H→L+1(2.0), H→L+2(7.22)
	3	3.5619	H-2→L+1(9.68), H-2→L+4(5.78), H-2→L+5(9.95), H-3→L+2(2.23)
	4	3.5814	H-1→L+2(3.38), H-1→L+3(3.92), H→L+1(2.67), H→L+3(2.42)
	10	4.1047	H-1→L+1(2.0), H-1→L+2(4.5), H→L(7.22), H→L+3(3.38)
	11	4.1674	**H-1→L(2.38), H→L(3.38), H→L+2(2.88), H→L+3(8.49), H→L+5(3.38)**
	12	4.2053	H-1→L(8.0), H-1→L+2(3.92), H-1→L+5(3.38), H→L+3(2.88),H→L+5(2.42)
	13	4.2449	H-2→L+2(23.12), H-2→L+3(4.5), H-1→L(2.42), H→L+6(2.0)

Table S14.The matched excited state that contain the same orbital transition components of S_1 of **TPTZPS** revealed by TDDFT calculations. (Triplet state with main ISC channels highlighted with bold letter).

Excited state	n	Energy (eV)	Transition configuration (Percent contribution)
S_n	1	4.0596	**H-1→L+1(3.38), H-1→L+2(7.22),H→L(7.22), H→L+1(15.68), H→L+2(56.18)**
T_n	1	3.3764	**H-1→L+2(7.22), H→L(2.42), H→L+2(36.98), H→L+3(2.00)**
	2	3.4372	H-2→L(10.58), H-2→L+1(9.68), H-2→L+2(2.0), H-2→L+3(11.52)
	3	3.4445	H-1→L+6(5.12), H→L+1(2.88), H→L+6(20.48), H→L+8(4.5)
	4	3.4663	H-1→L+1(7.22), H-1→L+3(2.88), H-1→L+5(4.5), H→L+5(3.38), H→L+9(2.42)
	8	3.9637	H-2→L(62.72), H-2→L+1(3.38), H-2→L+3(5.78), H-3→L(2.0), H→L(2.42)
	9	4.0423	H-1→L(20.48), H-1→L+4(10.58), H→L(10.58), H→L+4(5.12), H→L+5(5.78)
	10	4.1100	H-1→L(8.0), H-1→L+5(3.38), H→L(15.68), H→L+5(5.78),H→L+6(3.38)
	11	4.1531	**H-1→L+2(5.12), H-1→L+4(2.42), H→L+2(15.68), H→L+3(4.5)**

Table S15. The matched excited state that contain the same orbital transition components of S_1 of **TPTZPSe** revealed by TDDFT calculations. (Triplet state with main ISC channels highlighted with bold letter)

Excited state	n	Energy (eV)	Transition configuration (Percent contribution)
S_n	1	4.0270	**H-1→L(12.5),H→L(81.92)**
T_n	1	3.3614	H-1→L+1(6.48), H-1→L+2(16.82), H→L+1(2.88), H→L+2(14.58)
	2	3.4414	H-3→L(3.38), H-3→L+1(5.12), H-1→L(3.92), H→L+5(2.18)
	3	3.4442	H-3→L(3.38), H-3→L+1(2.33), H→L(2.0), H→L+1(2.42), H→L+6(3.92)
	4	3.4723	H-2→L+3(2.42), H-2→L+5(5.78),H→L+1(2.25), H→L+5(2.88)
	7	3.8611	**H-1→L(14.58), H→L(56.18)**
	8	3.9082	H-1→L(2.0), H-1→L+3(21.78), H→L+2(5.12), H→L+3(11.52), H→L+4(6.48)
	9	3.9596	H-3→L(38.82), H-3→L+1(4.88), H→L(5.78), H-1→L(9.68),H-2→L(6.48)
	10	4.0370	H-2→L(21.78), H-1→L(28.88), H→L(5.12)

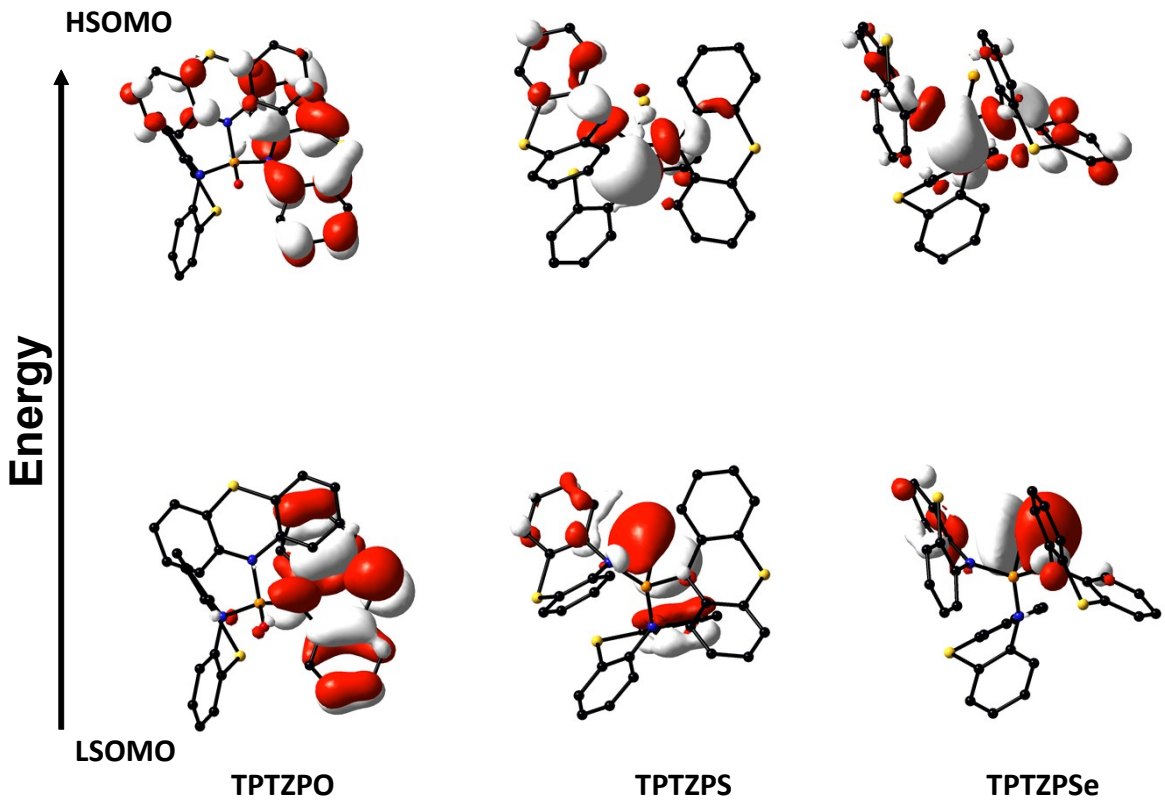


Figure S30: Frontier molecular orbital energy level diagram of **TPTZPO**, **TPTZPS** and **TPTZPSe** in S_1 state (DFT calculations using CAM-B3LYP functional with 6-31G(d,p) basis set).

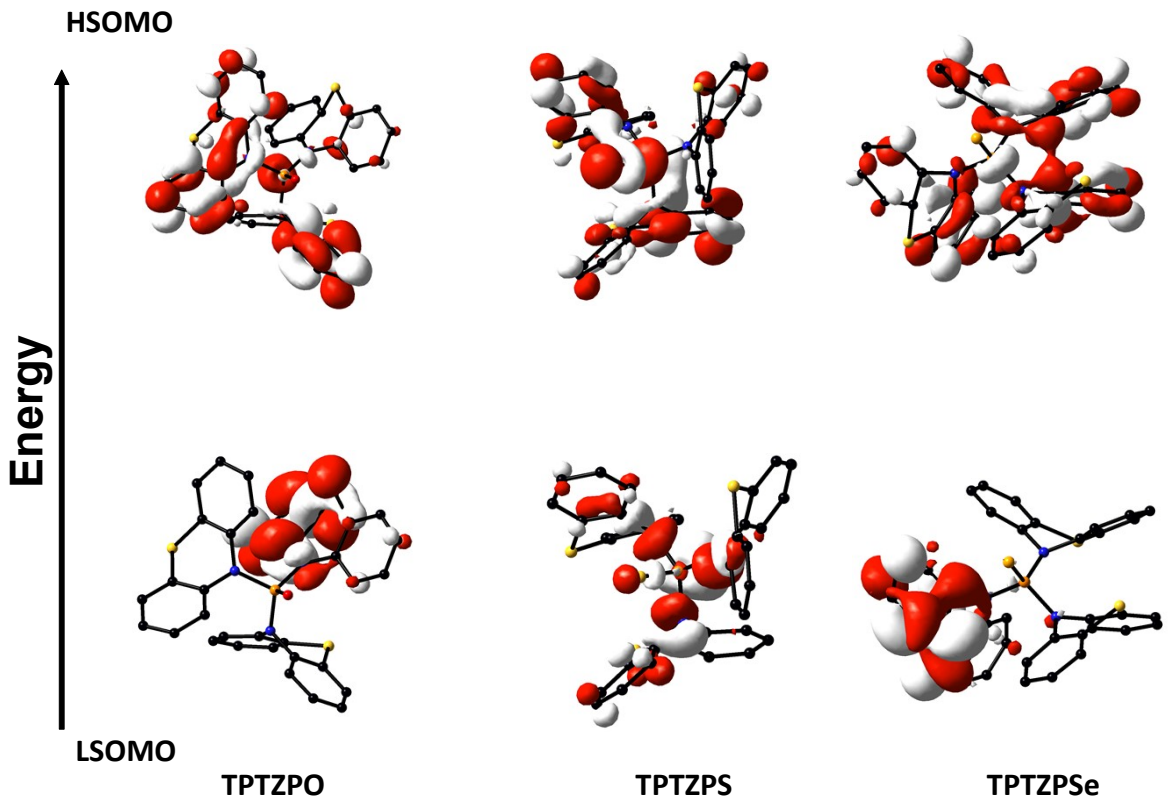


Figure S31: Frontier molecular orbital energy level diagram of **TPTZPO**, **TPTZPS** and **TPTZPSe** in T_1 state (DFT calculations using CAM-B3LYP functional with 6-31G(d,p) basis set).

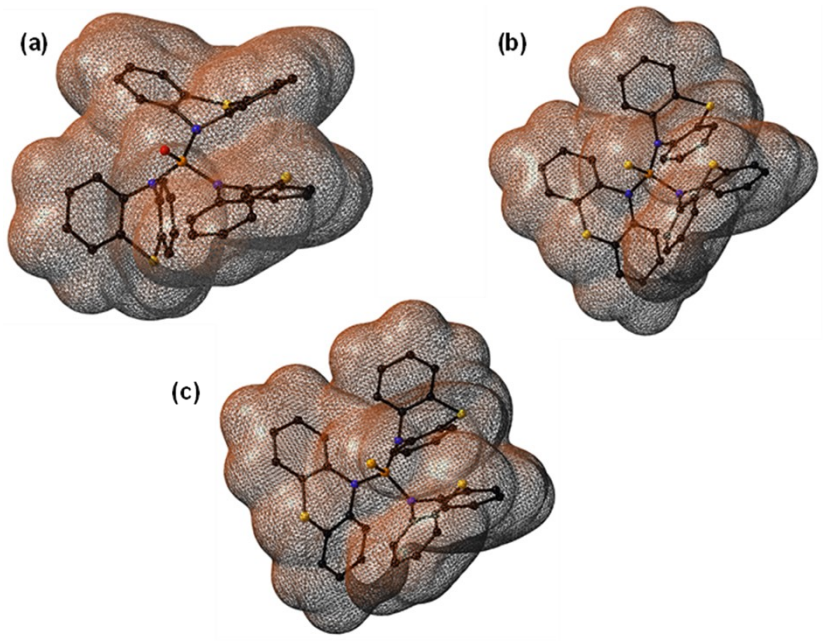


Figure S32: Ground state spin density pictures of (a) **TPTZPO**, (b) **TPTZPS** and (c) **TPTZPSe** calculated from optimized ground state geometry using CAM-B3LYP functional and 6-31g (d,p) basis set.

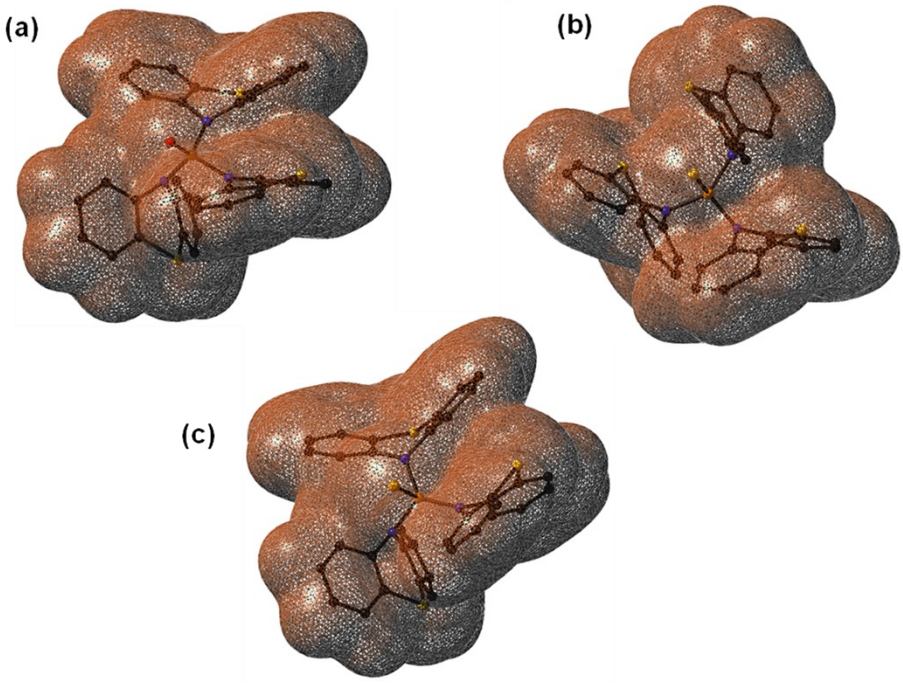


Figure S33: S_1state spin density pictures of (a) **TPTZPO**, (b) **TPTZPS** and (c) **TPTZPSe** calculated from optimized singlet state geometry using CAM-B3LYP functional and 6-31g (d,p) basis set.

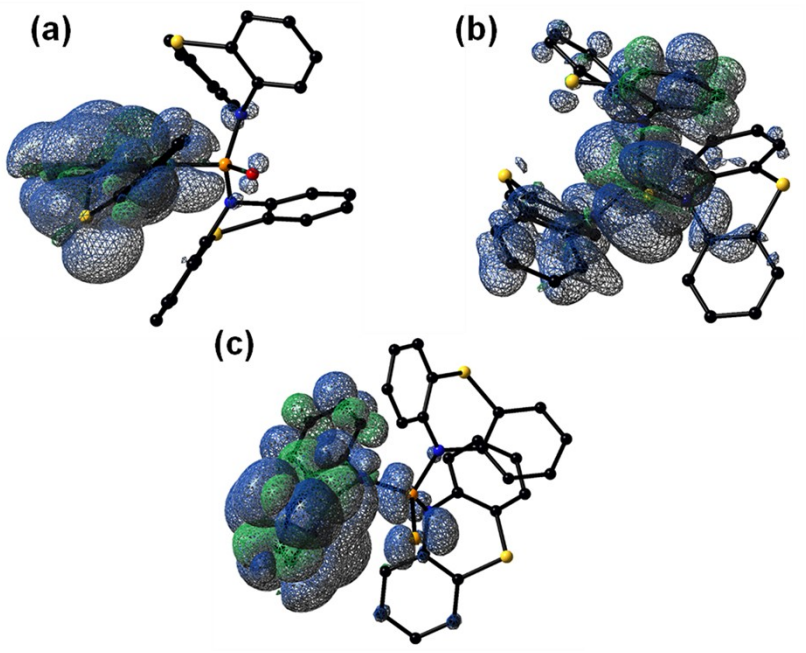


Figure S34: T_1 spin density pictures of (a) **TPTZPO**, (b) **TPTZPS** and (c) **TPTZPSe** calculated from optimized triplet state geometry using CAM-B3LYP functional and 6-31g (d,p) basis set.

References:

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