Supporting information for

Unveiling the Photophysical and Excited State Properties of Multi-Resonant OLED Emitters using Combined DFT and CCSD Method

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1. STEOM-DLPNO-CCSD Configuration Details:

The TD-DFT (as implemented in Gaussian 16) and DLPNO-STEOM-CCSD (as implemented in ORCA software) methods were used to figure out the excited state vertical excitation energies. The RIJCOSX approximation was used in the STEOM integral dressing step. Three roots were requested for lowest excited state S_1, T_1 and Six roots were requested for T_2 excited state using ORCA's "TightPNO" settings[1] following the default thresholds. Since the quality of the singles (diagonal) PNOs is especially important, these are generated as a separate set using a tighter than usual threshold of $T_{CutPNOSingles} = 6.6\times10^{10}$. The cutoff values for the natural orbital occupation numbers in the active space selection procedure for the occupied and virtual orbitals ("Othresh" and "Vthresh", respectively) were set to 5×10^{3} (Othresh, VThresh 1×10^{2} for few molecules).

During the calculation, **STEOMSOC** is set to true. To include the solvation effects, a conductor-like continuum solvation model (CPCM) with toluene solvent was used during the DLPNO-STEOM-CCSD calculations. From the above configurations, we achieved a percentage active character of 97.5% above for all the molecules and the HOMO to LUMO (H→L) orbital contribution reached above 93% for all the molecules. The below 97 percentage active character were resubmitted with Othresh and VThresh 1×10^{2} configuration reached 97.5%.[2] From the wave-function calculation results, we considered the SOC matrix elements and ΔE_{ST} values.

Table S1a. Optimally tuned ω values (in $Bohr^{-1}$) for the CzBX and CzBX2X molecules calculated at the ωB97XD/6-31+G(d) level. (here X=O, S and Se)

CzBX	**ω**	**CzBO2X**	**ω**	**CzBS2X**	**ω**	**CzBSe2X**	**ω**
CzBO	0.1507	CzBO2O	0.1555	CzBS2O	0.1525	CzBSe2O	0.1516
CzBS	0.1487	CzBO2S	0.1494	CzBS2S	0.1465	CzBSe2S	0.1459
CzBSe	0.1492	CzBO2Se	0.1477	CzBS2Se	0.1449	CzBSe2Se	0.1434

Table S1b. CzBX molecules structural relaxation (in eV) between S_1 and T_1 state optimized geometries.

Molecules	Structural relaxation ($S_1 \leftrightarrow T_1$)
CzBO	0.00319
CzBS	0.00430
CzBSe	0.00914

Table S1c. Intramolecular Reorganization Energy and root mean square deviation between S_1 and T_1 state optimized geometries.

Molecules	λ_{intra} (eV)	RMSD (Å)
CzBO	0.004	0.014
CzBS	0.006	0.020
CzSe	0.003	0.041

Table S1d: Comparison of lowest energy optical absorption (in eV) with 6-31G(d) and 6-31+G(d) basis sets.

Molecules	*Expt.[Ref.3]*	*ω**B97XD/ 6-31G(d)	*ω**B97XD/ 6-31+G(d)	*Combined DFT and CCSD*
CzBO	2.910	3.472 *f*=0.445	3.427 *f*=0.455	2.938 *f*=0.342
CzBS	2.774	3.318 *f*=0.407	3.272 *f*=0.413	2.806 *f*=0.317
CzBSe	2.749	3.226 *f*=0.383	3.210 *f*=0.383	2.755 *f*=0.288
MAD	0	0.527	0.492	**0.022**

Here, MAD is the mean absolute deviations. MAD is generally lower for higher basis set. Thus, we consider 6-31+G(d) basis set for single-point calculations. Also, we it is well know that the higher basis sets do not much affect the geometry. However, in this study, we mostly focus on combined DFT and CCSD method (see Table 2). In our combined DFT and CCSD method, we used OT-SRSH-ωB97XD/6-31G(d)/LANL2DZ level of theory for geometry optimization and STEOM-DLPNO-CCSD/def2-TZVP level of theory for single-point energy calculation.

Table S2. HOMO, LUMO, energy gap ($\Delta E_{H\text{-}L}$) of CzBX and CzBX2X series in eV using combined DFT-CCSD method.

Molecules	E_{HOMO}	E_{LUMO}	$\Delta E_{H\text{-}L}$
CzBO	-7.537	1.183	8.720
CzBS	-7.421	1.111	8.532
CzBSe	-7.408	1.081	8.489
CzBO2O	-7.551	1.287	8.838
CzBO2S	-7.097	1.187	8.285
CzBO2Se	-7.163	1.106	8.269
CzBS2O	-7.338	1.213	8.551
CzBS2S	-7.000	1.081	8.080
CzBS2Se	-7.058	0.999	8.058
CzBSe2O	-7.287	1.169	8.456
CzBSe2S	-7.016	1.017	8.033
CzBSe2Se	-7.077	0.933	8.010

Table S3. Optical energy orbital absorption and emission energies configurations obtained using STEOM-DLPNO-CCSD.

Molecules	λ_{abs} ($S_0 \rightarrow S_1$)		λ_F ($S_1 \rightarrow S_0$)	
	Orbital Contribution	Percentage	Orbital Contribution	Percentage
CzBO	H→L	94	H→L	93
CzBS	H→L	94	H→L	94
CzBSe	H→L	94	H→L	94
CzBO2O	H→L	92	H→L	95
CzBO2S	H→L	93	H→L	94
CzBO2Se	H→L	94	H→L	94
CzBS2O	H→L	93	H→L	94
CzBS2S	H→L	93	H→L	94
CzBS2Se	H→L	93	H→L	94
CzBSe2O	H→L	93	H→L	96
CzBSe2S	H→L	95	H→L	95
CzBSe2Se	H→L	94	H→L	94

Table S4. Wavelengths for lowest energy optical absorption, fluorescence and phosphorescence energies (in nm) for CzBX and CzBX2X molecules.

Molecules	λ_{abs} ($S_0 \rightarrow S_1$)		λ_F ($S_1 \rightarrow S_0$)		λ_P ($T_1 \rightarrow S_0$)	
	[3]Exp.	Theory	[3]Exp.	Theory	[3]Exp.	Theory
CzBO	426	422.0 (*f*=0.3415)	445	446.4 (*f*=0.2985)	471	472.7
CzBS	447	441.8 (*f*=0.3169)	471	468.3 (*f*=0.2803)	491	489.1
CzBSe	451	450.0 (*f*=0.2881)	477	476.0 (*f*=0.2666)	499	494.1
CzBO2O	-	424.4 (*f*=0.1969)	-	529.2 (*f*=0.1719)	-	539.0
CzBO2S	-	475.8 (*f*=0.1965)	-	524.0 (*f*=0.1649)	-	530.0
CzBO2Se	-	475.8 (*f*=0.1938)	-	519.4 (*f*=0.1638)	-	522.2
CzBS2O	-	446.3 (*f*=0.2239)	-	517.6 (*f*=0.2049)	-	548.9
CzBS2S	-	499.2 (*f*=0.1940)	-	542.7 (*f*=0.1884)	-	564.0
CzBS2Se	-	502.3 (*f*=0.1987)	-	545.3 (*f*=0.1696)	-	556.3
CzBSe2O	-	455.7 (*f*=0.2371)	-	501.4 (*f*=0.2636)	-	547.2
CzBSe2S	-	500.6 (*f*=0.2069)	-	552.7 (*f*=0.1766)	-	575.7
CzBSe2Se	-	503.7 (*f*=0.2061)	-	550.5 (*f*=0.1781)	-	565.0

Table S5a. Calculation of k_{RISC} (in s^{-1}) for CzBX molecules with λ_M=0.1 eV and λ_M=0.2 eV and considering Huang-Rhys (S) factor equals to zero.

Molecules	λ_{intra} (eV)	Huang-Rhys (S) factor equal to 0.	k_{RISC} with λ_M=0.1 eV	k_{RISC} with λ_M=0.2 eV
CzBO	0.004	0	2.46×10^4	1.26×10^4
CzBS	0.006	0	1.90×10^6	9.48×10^5
CzBSe	0.003	0	9.87×10^7	4.10×10^7

Table S5b. Calculation of k_{RISC} (in s^{-1}) for CzBX molecules with λ_M=0.1 eV and λ_M=0.2 eV and considering Huang-Rhys (S) factor.

Molecules	λ_{intra} (eV)	Huang-Rhys (S) factor	Effective frequency, ω in cm^{-1}	k_{RISC} with λ_M=0.1 eV	k_{RISC} with λ_M=0.2 eV
CzBO	0.004	0.036	1353.25	2.38×10^4	1.19×10^4
CzBS	0.006	0.023	1427.01	1.86×10^6	9.26×10^5
CzBSe	0.003	0.032	1400.56	9.21×10^7	3.98×10^7

The total reorganization energy is combination of intramolecular reorganization and solvent (environmental) reorganization energy ($\lambda_{tot}=\lambda_{intra} + \lambda_{sol}$). The contribution to the λ_{intra} by each normal mode is given by the following equation.

$$\lambda_{intra} = \sum \lambda_i = \sum \hbar\omega_i S_i$$

Where, S_i is the Huang-Rhys factor and ω_i the frequency for i^{th} normal mode. When the contribution to the λ_{intra} is due to only a few (n) effective normal modes,

$$S_{eff} = \sum_n S_n$$

$$\omega_{eff} = \frac{\sum_n S_n \times \omega_n}{\sum_n S_n}$$

Table S5c. Calculated k_{ISC} and k_{RISC} rate constants (in s^{-1}) considering Marcus reorganization energy (λ_M) equals to 0.1 and 0.2 eV, respectively.

Molecules	λ_M=0.1 eV		λ_M=0.2 eV	
	Tot k_{ISC}	Tot k_{RISC}	Tot k_{ISC}	Tot k_{RISC}
CzBO	5.29×10^6	2.46×10^4	0.4×10^7	1.26×10^4
CzBS	1.17×10^8	1.90×10^6	0.6×10^8	9.48×10^5
CzBSe	5.07×10^9	9.87×10^7	2.11×10^9	0.41×10^8
CzBO2O	4.00×10^6	9.24×10^5	1.17×10^6	2.70×10^5
CzBO2S	4.25×10^4	3.78×10^3	1.20×10^4	1.13×10^3
CzBO2Se	1.27×10^5	3.40×10^4	3.42×10^4	9.35×10^3
CzBS2O	6.32×10^6	3.06×10^4	4.22×10^6	2.04×10^4
CzBS2S	1.32×10^4	2.62×10^2	5.14×10^3	1.02×10^2
CzBS2Se	3.06×10^6	6.38×10^6	9.04×10^5	2.41×10^5
CzBSe2O	2.32×10^8	1.95×10^5	1.90×10^8	4.06×10^5
CzBSe2S	5.18×10^4	1.21×10^3	2.09×10^4	5.02×10^2
CzBSe2Se	4.40×10^6	5.70×10^5	1.41×10^6	1.79×10^5

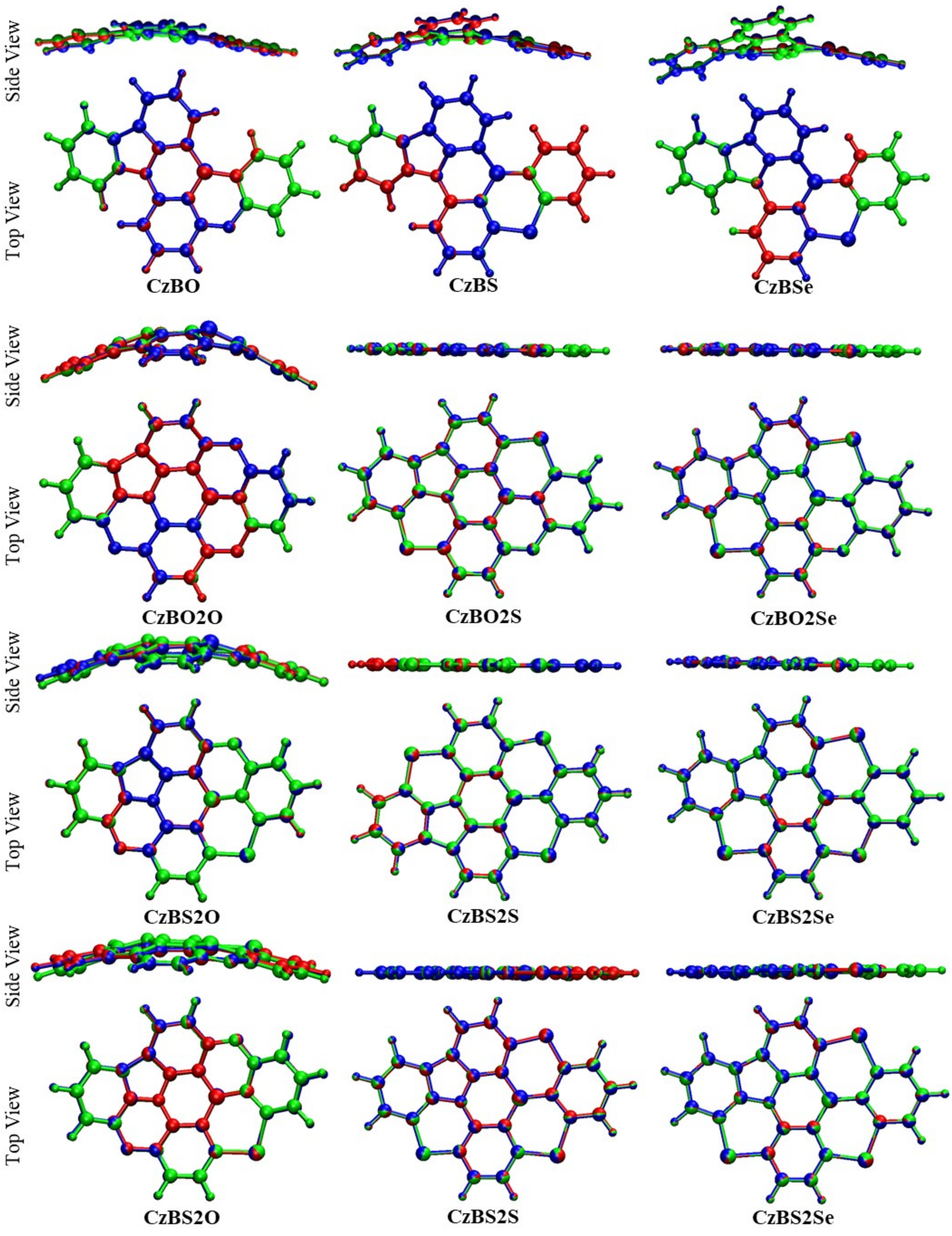

Figure S1. Excited states optimized structures (S_1 is blue color, T_1 is red color & T_2 is green color)

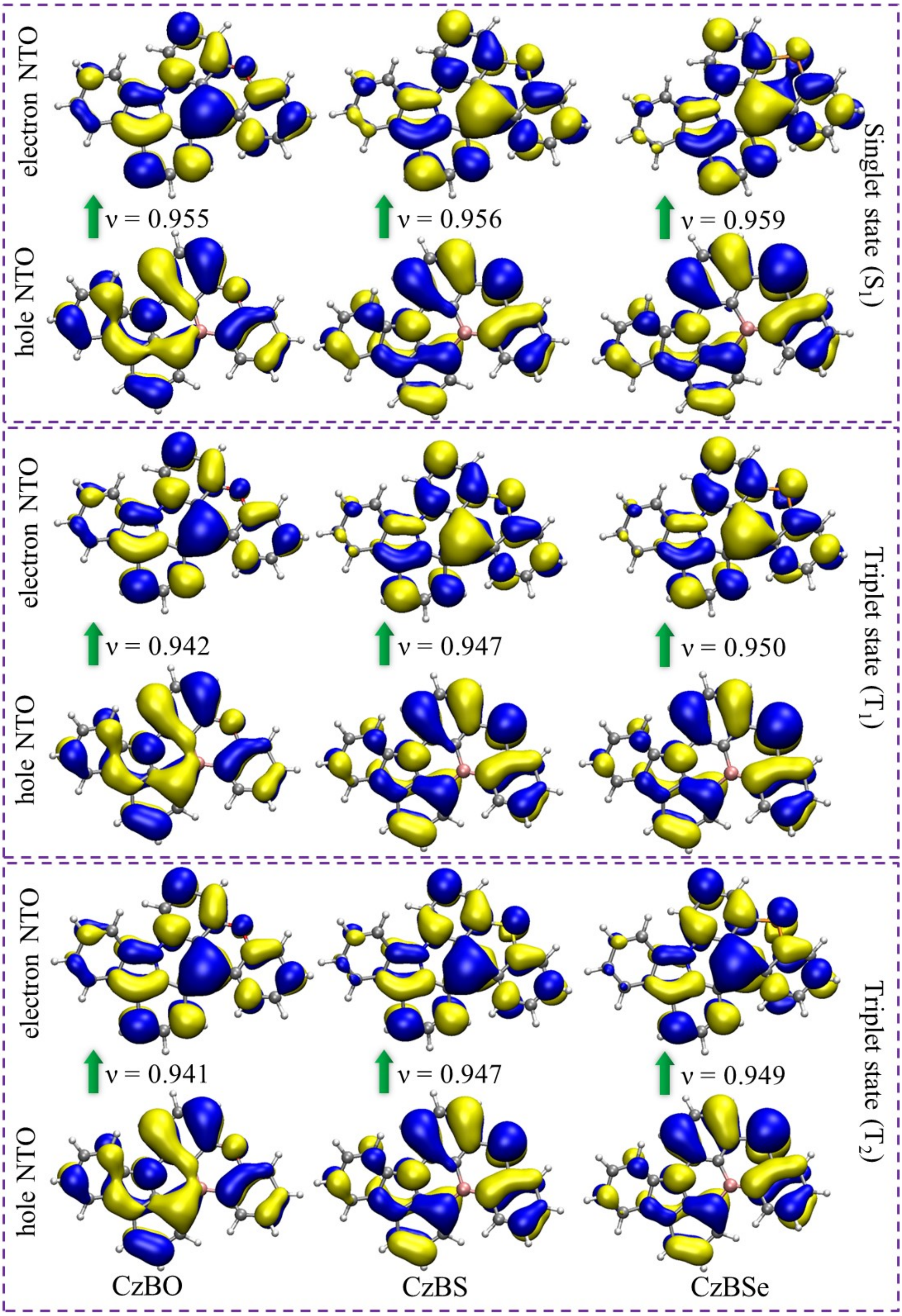

Figure S2. NTOs of CzBX series of molecules for their the S_1, T_1 and T_2 states at their respective optimized geometries. The hole NTO and electron NTO (isovalue = 0.02 au) with the largest weight, ν, are illustrated below and above the arrows, respectively. NTOs are calculated at OT-SRSH-ωB97XD/6-31+G* level theory for all the molecules.

Table S6. Calculated excited states (S_1, T_1 & T_2) chalcogens atom distance with carbon atom all values in Å.

Molecules	eXa ($S_1/T_1/T_2$)	eXb ($S_1/T_1/T_2$)	eXc ($S_1/T_1/T_2$)	eXd ($S_1/T_1/T_2$)	eXe ($S_1/T_1/T_2$)	eXf ($S_1/T_1/T_2$)
CzO	1.354/1.356/1.355	1.375/1.373/1.373				
CzS	1.754/1.753/1.753	1.763/1.76/1.76	-	-	-	-
CzSe	1.879/1.874/1.874	1.886/1.881/1.881				
CzO2O	1.37/1.373/1.374	1.403/1.399/1.4	1.376/1.382/1.382	1.377/1.39/1.372	1.395/1.372/1.391	1.399/1.4/1.402
CzO2S	1.363/1.365/1.372	1.398/1.395/1.383	1.762/1.768/1.735	1.76/1.758/1.754	1.806/1.805/1.786	1.82/1.819/1.8
CzO2Se	1.359/1.36/1.361	1.389/1.387/1.389	1.922/1.929/1.924	1.923/1.921/1.916	1.974/1.974/1.968	1.987/1.987/1.981
CzS2O	1.778/1.777/1.796	1.808/1.809/1.799	1.38/1.384/1.387	1.377/1.372/1.399	1.387/1.382/1.367	1.3951.397/1.398
CzS2S	1.758/1.758/1.779	1.786/1.787/1.781	1.755/1.762/1.779	1.757/1.752/1.796	1.782/1.78/1.739	1.799/1.799/1.795
CzS2Se	1.75/1.749/1.748	1.774/1.744/1.773	1.916/1.923/1.918	1.921/1.918/1.912	1.948/1.946/1.940	1.965/1.964/1.958
CzSe2O	1.952/1.952/1.966	1.987/1.989/1.97	1.38/1.383/1.386	1.379/1.374/1.399	1.384/1.379/1.363	1.392/1.395/1.397
CzSe2S	1.924/1.923/1.918	1.954/1.955/1.95	1.752/1.758/1.758	1.757/1.751/1.75	1.774/1.772/1.771	1.791/1.791/1.79
CzSe2Se	1.915/1.913/1.909	1.942/1.941/1.937	1.912/1.919/1.1914	1.921/1.918/1.913	1.939/1.937/1.932	1.958/1.957/1.952

Here red accent is bond distance between Oxygen atom and nearest Carbon atom d(O-C), yellow is d(S-C), Orange is d(Se-C). see **Figure 4**.

Table S7. Calculated emission rate k_F and k_P at 300° temperature.

Molecules	k_F (s^{-1})	k_P (s^{-1})			
		T_1	T_2	T_3	Tot. k_P
CzBO	1.74×10^8	0.26×10^1	0.28×10^1	0.14×10^1	2.28
CzBS	1.51×10^8	5.03×10^2	3.33×10^1	0.11×10^1	1.79×10^2
CzBSe	1.46×10^8	5.94×10^2	1.47×10^3	1.98×10^1	6.96×10^2
CzBO2O	1.14×10^8	0	0	0.54×10^1	1.81
CzBO2S	9.00×10^7	1.81×10^1	2.73×10^1	0	1.52×10^1
CzBO2Se	9.13×10^7	7.35×10^2	1.91×10^3	3.17×10^3	1.94×10^3
CzBS2O	1.22×10^8	5.22×10^1	8.03×10^1	2.54×10^1	5.26×10^1
CzBS2S	9.24×10^7	3.25×10^1	1.38×10^1	0	1.54×10^1
CzBS2Se	8.51×10^7	1.41×10^3	3.40×10^1	4.91×10^2	6.43×10^2
CzBSe2O	1.42×10^8	2.41×10^4	3.72×10^2	1.50×10^3	8.65×10^3
CzBSe2S	8.62×10^7	4.84×10^4	5.60×10^2	2.41×10^1	1.63×10^4
CzBSe2Se	8.33×10^7	1.64×10^3	2.92×10^1	9.10×10^2	8.61×10^2

The average phosphorescence rate constant was calculated using the following equation:

$$k_{ph}^{av} = \frac{k_1 + k_2 + k_3}{3}$$

The zero-field splitting (ZPS) was not significant and neglected for the calculation of average phosphorescence rate constant.

References

(1) D. G. Liakos, M. Sparta, M. K. Kesharwani, J. M. L. Martin and F. Neese, *J. Chem. Theory Comput*., 2015, **11**, 1525–1539.

(2) B. Kozma, R. Berraud-Pache, A. Tajti, P. G. Szalay, *Mol. Phys.* 2020, **118**, e1776903.

(3) I. S. Park, H. Min and T. Yasuda, *Angew. Chem. Int. Ed.* 2022, **134**, e202205684.