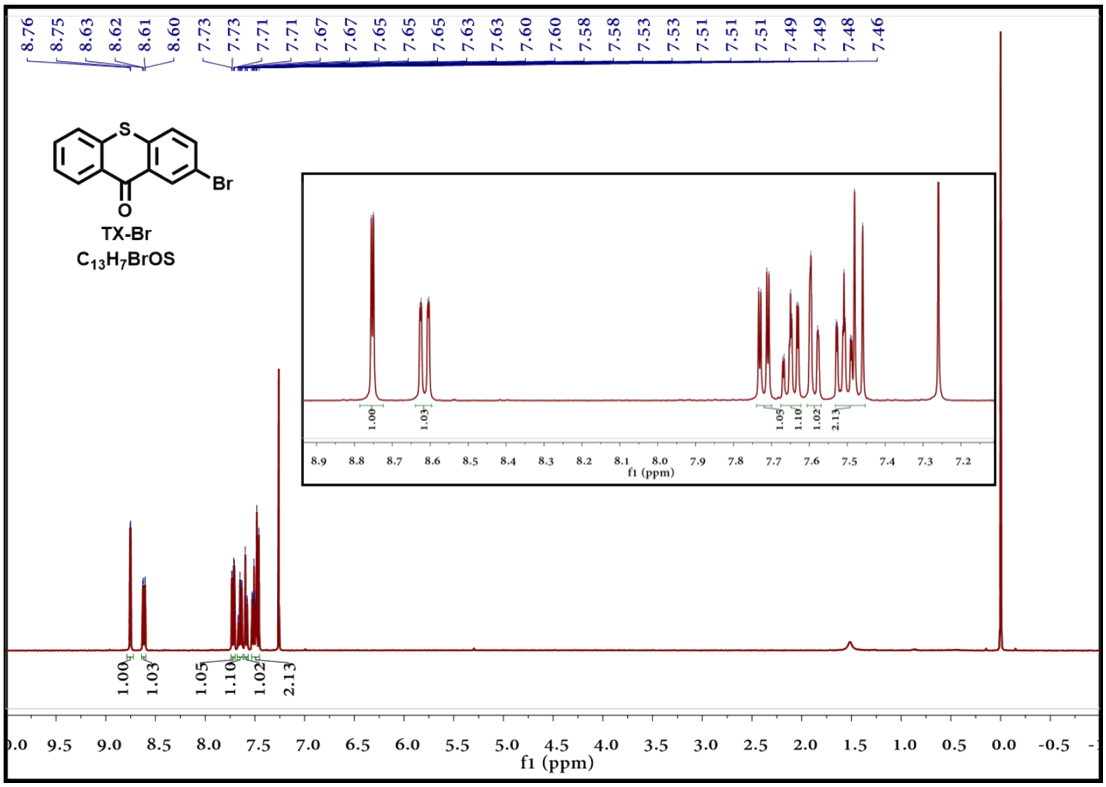
Supporting Information

Highly Efficient Purely Organic Room-Temperature Phosphorescence Film based on a Selenium-Containing Emitter for Sensitive Oxygen Detection

Shuai Wang, Haiyang Shu, Xianchao Han, Xiaofu Wu, Hui Tong, Lixiang Wang**

1. Experimental details

(a)



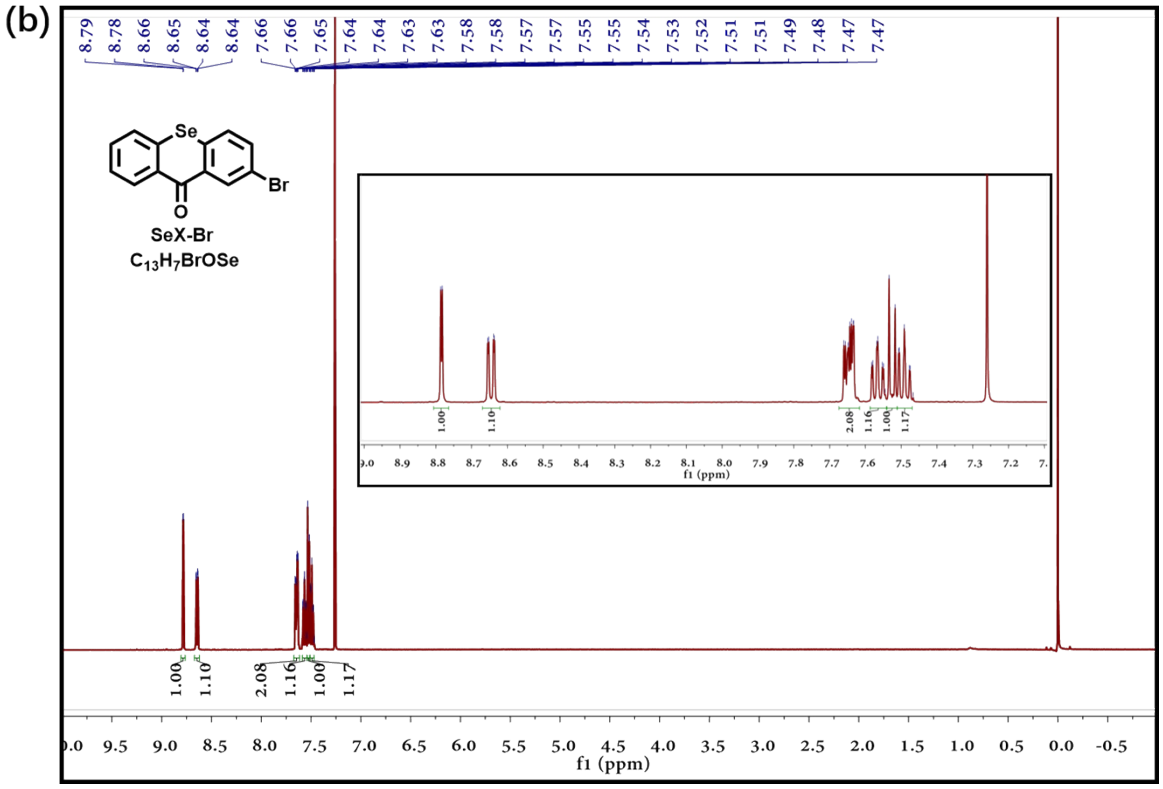
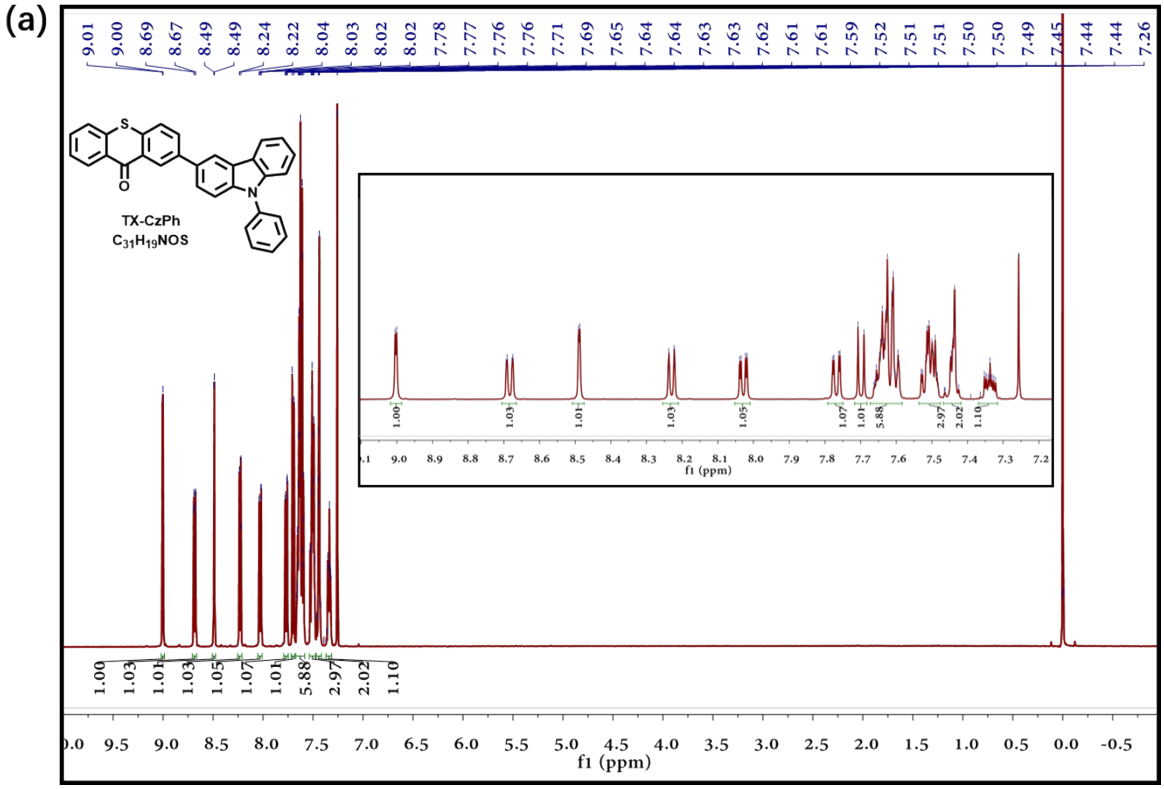


Figure S1. ^{1}H NMR of TX-Br (a) and SeX-Br (b)



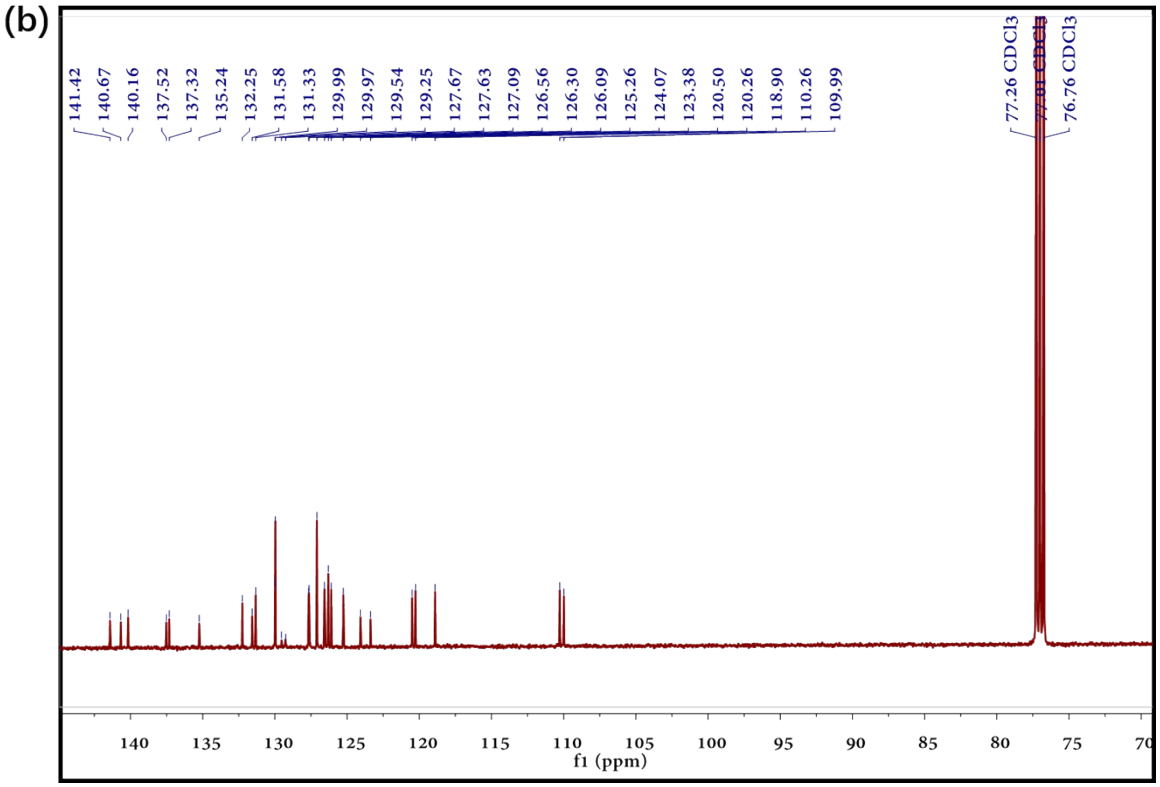
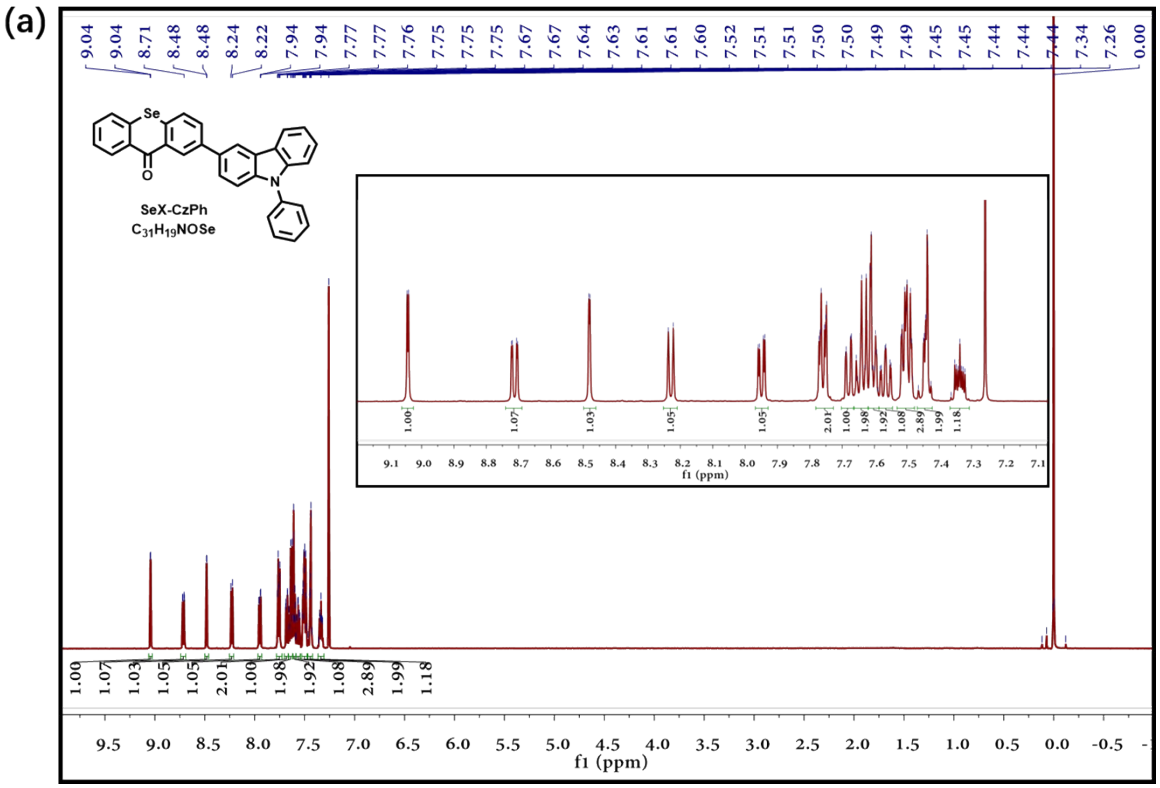


Figure S2. ^{1}H NMR (a) and ^{13}C NMR (b) of TX-CzPh



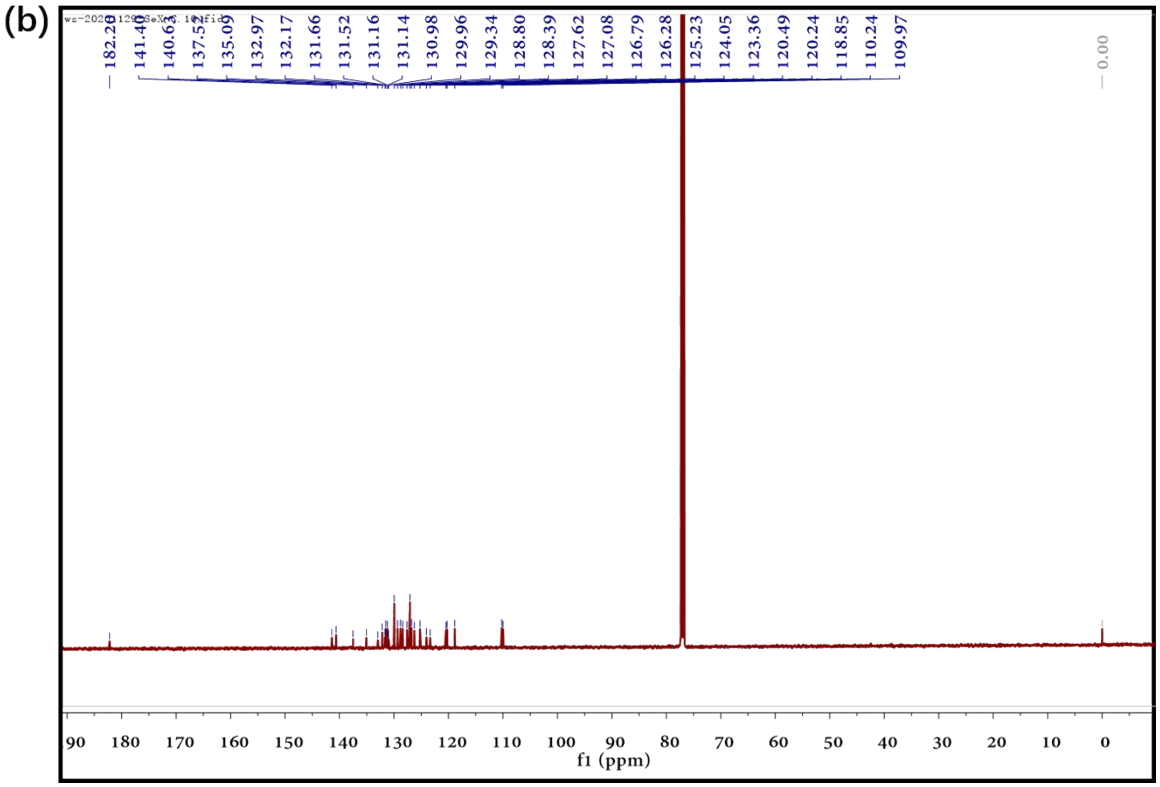


Figure S3. ^{1}H NMR (a) and ^{13}C NMR (b) of SeX-CzPh

2. Photophysical measurements

The radiative rate constants of fluorescence (k_r^F), phosphorescence (k_r^P), the intersystem crossing rate constant (k_{ISC}), and the sum of the nonradiative constant of phosphorescence (k_{nr}^P) and quenching rate of T_1 (k_q) of SeX-CzPh and TX-CzPh were calculated according to the following equations:

$$\Phi_{FL} = 1 - \Phi_{ISC} - \Phi_{nr}^F \quad \text{(S1)}$$

$$\Phi_{Ph} = \Phi_{ISC} - \Phi_{nr}^P - \Phi_q \quad \text{(S2)}$$

$$k_r^F = \frac{\Phi_{FL}}{\tau_{FL}} \quad \text{(S3)}$$

$$k_{ISC} = \frac{\Phi_{ISC}}{\tau_{FL}} \quad \text{(S4)}$$

$$\frac{1}{\tau_{FL}} = k_r^F + k_{nr}^F + k_{ISC} \quad \text{(S5)}$$

$$\Phi_{FL} = \frac{k_r^F}{k_r^F + k_{nr}^F + k_{ISC}} \quad \text{(S6)}$$

$$\frac{1}{\tau_{Ph}} = k_r^P + k_{nr}^P + k_q \quad \text{(S7)}$$

$$\Phi_{Ph} = \frac{\Phi_{ISC} k_r^P}{k_r^P + k_{nr}^P + k_q} \quad \text{(S8)}$$

where Φ_{FL}, Φ_{Ph} and Φ_{ISC} are the absolute quantum yield of fluorescence, phosphorescence and intersystem crossing, and Φ_{nr}^F and Φ_{nr}^P is the nonradiative absolute quantum yield of fluorescence and phosphorescence, and k_q is the quenching absolute quantum yield of T_1, and $\tau_{FL}$and τ_{Ph} are the average lifetime of fluorescence and phosphorescence, and k_{nr}^F is the nonradiative constant of fluorescence. The quantum yield of the intersystem crossing (Φ_{ISC}) could be assumed to be $1 - \Phi_{FL}$ according to the following equations (S1) and (S2), since both SeX-CzPh and TX-CzPh showed intense phosphorescence emission with negligible fluorescence emission in 2-methyltetrahydrofuran solutions at 77 K.[1-2, 5]

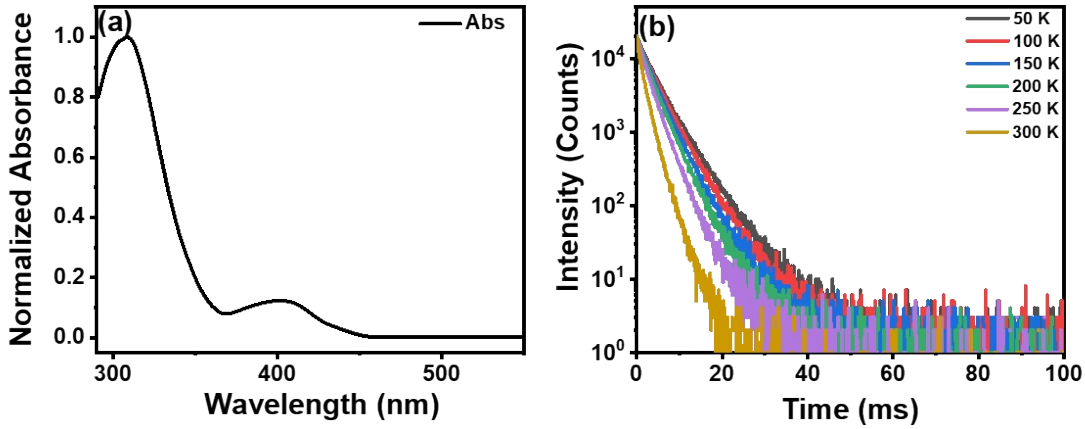


Figure S4. (a) UV-vis spectra of SeX-CzPh in toluene and (b) temperature-dependent time-resolved PL decay spectra of SeX-CzPh doped film at 500 nm.

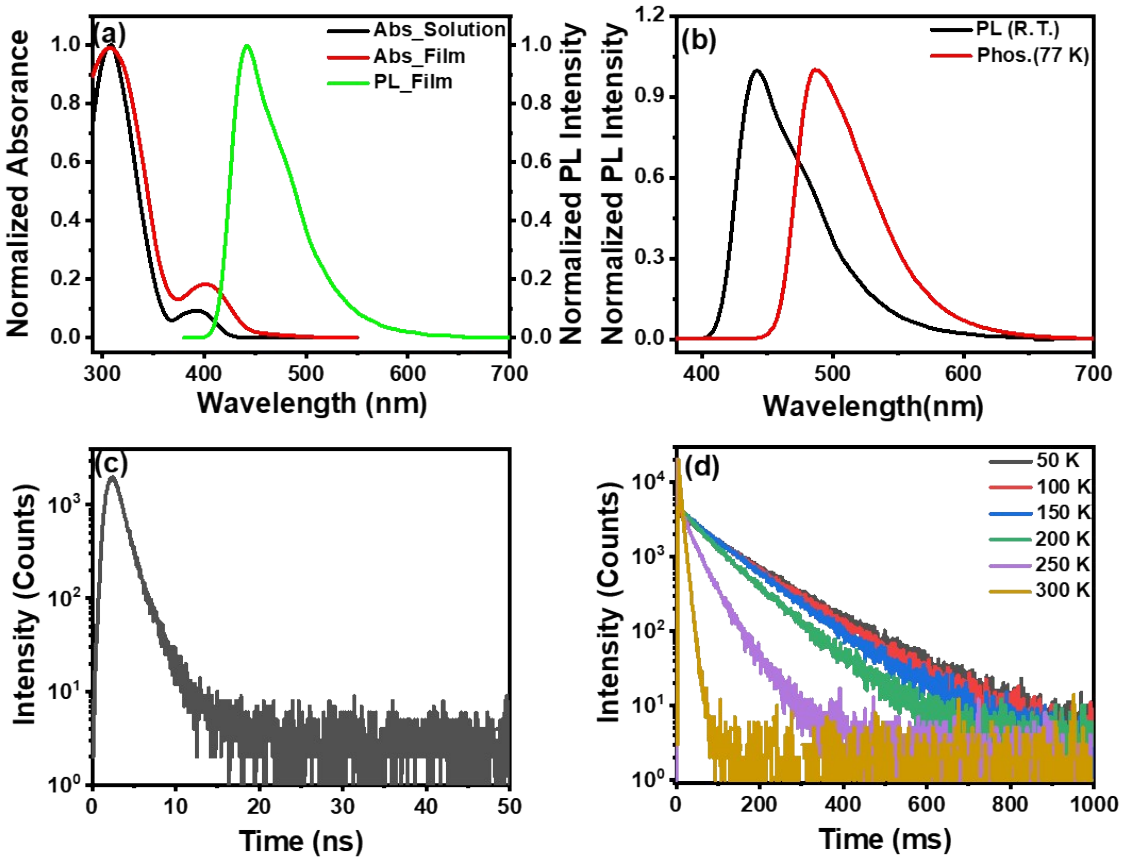


Figure S5. (a) UV-vis spectra of TX-CzPh in toluene (black) and doped film (red) and steady-state PL spectra of TX-CzPh doped film (green) at room temperature; (b) steady-state PL (black) at room temperature and delay spectra (red) at 77 K (delay time: 1 ms) of TX-CzPh doped film; (c) time-resolved PL decay spectra measured at 441 nm of TX-CzPh doped film at room temperature; (d) temperature-dependent time-resolved PL decay spectra of TX-CzPh doped film at 487 nm.

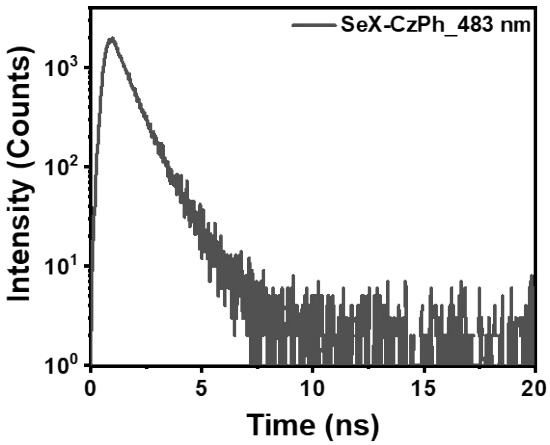


Figure S6. Time-resolved PL decay spectra measured at 483 nm of SeX-CzPh crystal powder at room temperature

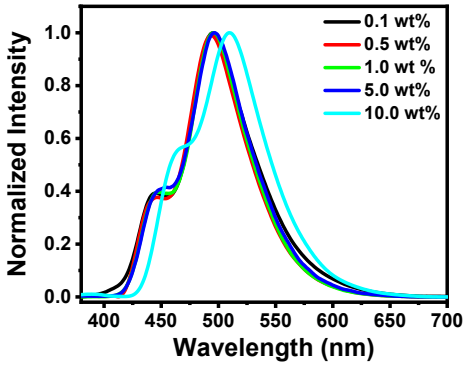


Figure S7. Steady-state PL spectra of SeX-CzPh doped film with different doping concentrations

The PLQY of 0.1 wt%, 0.5 wt%, 1 wt%, 5 wt% and 10 wt% SeX-CzPh doped films in vacuum at room temperature are 47.9%, 47.6%, 48.1%, 46.9% and 39.8%, respectively.

Table S1. Summary of phosphorescent quantum yields of organic RTP mertials doped films

Compound	Host	λ_{PL} [nm]	Φ_{Ph} [%]	Ref
DPTZ-DBT	Zeonex	540	60	1
4	β -estradiol	550	50	2
SeX-CzPh	PS	500	44.3	This work
HTO	PVA	467	44	3
2a	Zeonex	554	39.5	4
PSe2	DPEPO	500	35	5
PVA-100-2-HC-1	PVA	470	29.2	6
TX-CzPh	PS	487	10.1	This work
I-BF2dbm-OCH3	PMMA	517	4.5	7
TXCl	PMMA	487	0.95	8

Table S2. Summary of the photophysical properties of SeX-CzPh and TX-CzPh

	State	λ_{PL} [nm]	Φ_{PL} [%]	Φ_{FL} [%]	Φ_{Ph} [%]	τ_{FL} [ns]	τ_{Ph} [ms]	k_r^F [10^7 s^{-1}]	k_{ISC} [10^8 s^{-1}]	k_r^p [10^2 s^{-1}]	$k_{nr}+k_q$ [10^3 s^{-1}]
SeX-CzPh	Doped Film	453, 500	48.1	3.8	44.3	1.08	1.62	3.5	8.9	2.8	0.3
	Crystal Powder	481, 544	5.0	2.1	2.9	0.79	0.016	2.6	12.4	18.9	61.7
TX-CzPh	Doped Film	441, 487	21.9	11.8	10.1	1.35	10.35	8.7	6.5	0.1	0.9
	Crystal Powder	472, 529	29.3	7.6	21.7	1.21	0.61	6.3	7.7	3.9	1.3

Table S3 Photophysical properties of TX-CzPh and SeX-CzPh

	TX-CzPh[a]		SeX-CzPh[a]		SeX-CzPh[b]	
λ_{em}	441 nm	487 nm	451 nm	500 nm	483 nm	543 nm
τ_{avg}	1.35 ns	10.31 ms	1.08 ns	1.65 ms	0.79 ns	15.74 μs
τ_1		1.88 ms (8.2 %)		0.07 ms (3.4 %)		15.24 μs (99.5%)
τ_2		7.76 ms (53.5 %)		0.86 ms (34.4 %)		533.12 μs (0.5%)
τ_3		15.71 ms (38.3 %)		2.12 ms (62.2 %)		

[a] doped film. [b] crystal powder

3. Oxygen Sensing

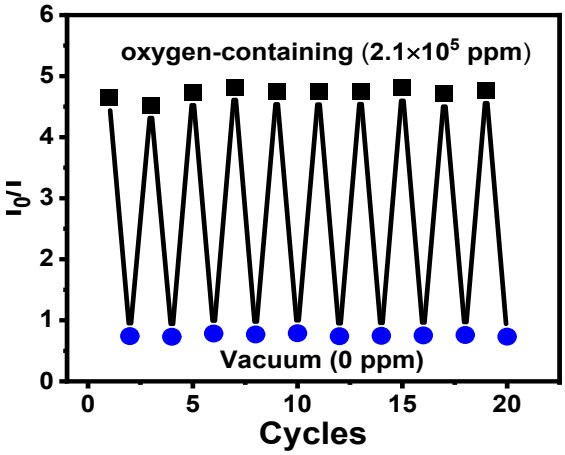


Figure S8. Reversible oxygen response of the TX-CzPh doped film

Table S4. Summary of the oxygen sensing properties of some phosphorescent materials

Probe	Linear [10^4 ppm]	$K_{SV}\times10^{-4}$ [ppm^{-1}]	LOD[a] [ppm]	R^2	Test method	Ref
SeX-CzPh	0-21	1.27	4.9	0.997	PL Intensity	This work
TX-CzPh	0-4	1.08	10.7	0.994	PL Intensity	This work
TBBU	0-21	1.26	5.0	0.998	Lifetime	9
SNPs	0-3	1.92	3.3	0.994	PL Intensity	10
2FT	0-0.3	5.32	1.2	0.999	PL Intensity	11
4FT	0-0.3	4.04	1.6	0.977	PL Intensity	
Lu-DVDMS	0-1	0.062	100.4	-	PL Intensity	12
Cu(POP)phencarz]-BF4–PS	0-100	0.15	41.7	0.997	PL Intensity	13
Pd-Al LDHs/Pd-TCPP	0-100	0.008	777.9	0.972	PL Intensity	14

4. X-ray crystallographic analysis

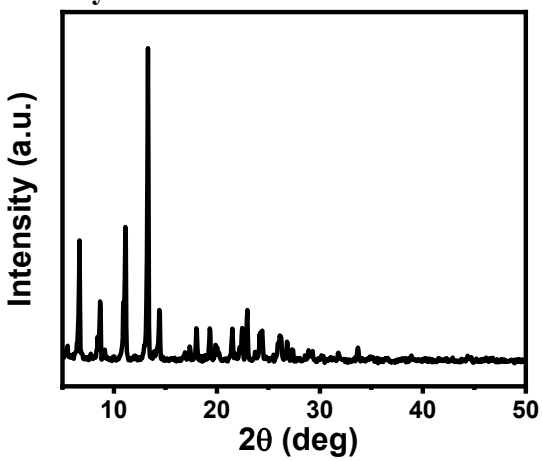


Figure S9. Powder X-ray diffraction patterns of SeX-CzPh crystal powder

Table S5. Single crystal Data of SeX-CzPh

Name	SeX-CzPh
Empirical formula	$C_{31}H_{19}NOSe$
Formula weight	500.43
Temperature	301(2)
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 4.0113(4) alpha = 90.00 b = 20.9812(19) beta = 94.065 c = 25.560 (2) gamma = 90.00
Volume	2145.8(4)
Z	4
Density	1.549
F (000)	1016.0
Radiation	Mo Kα radiation (λ =0.71073 Å)
Cell measurement theta min	2.5858
Cell measurement theta max	27.7594

5. Theoretical calculation results

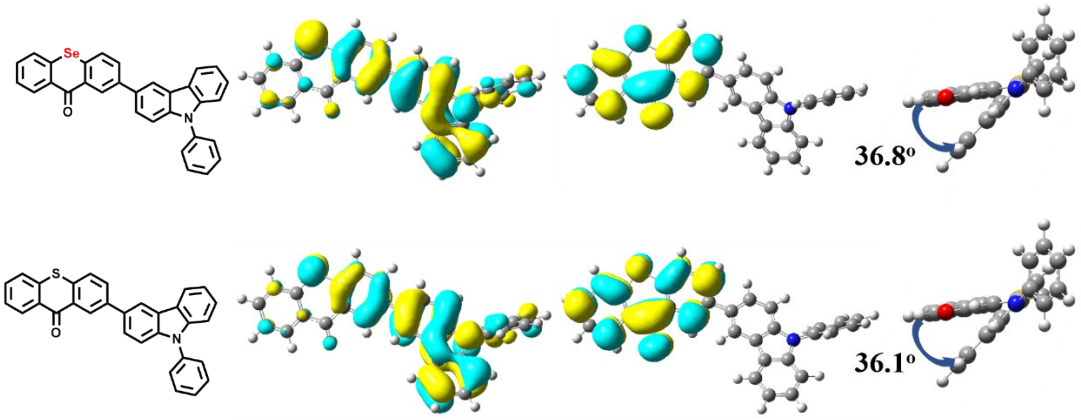


Figure S10. The molecular orbital distributions and the dihedral angles of SeX-CzPh and TX-CzPh

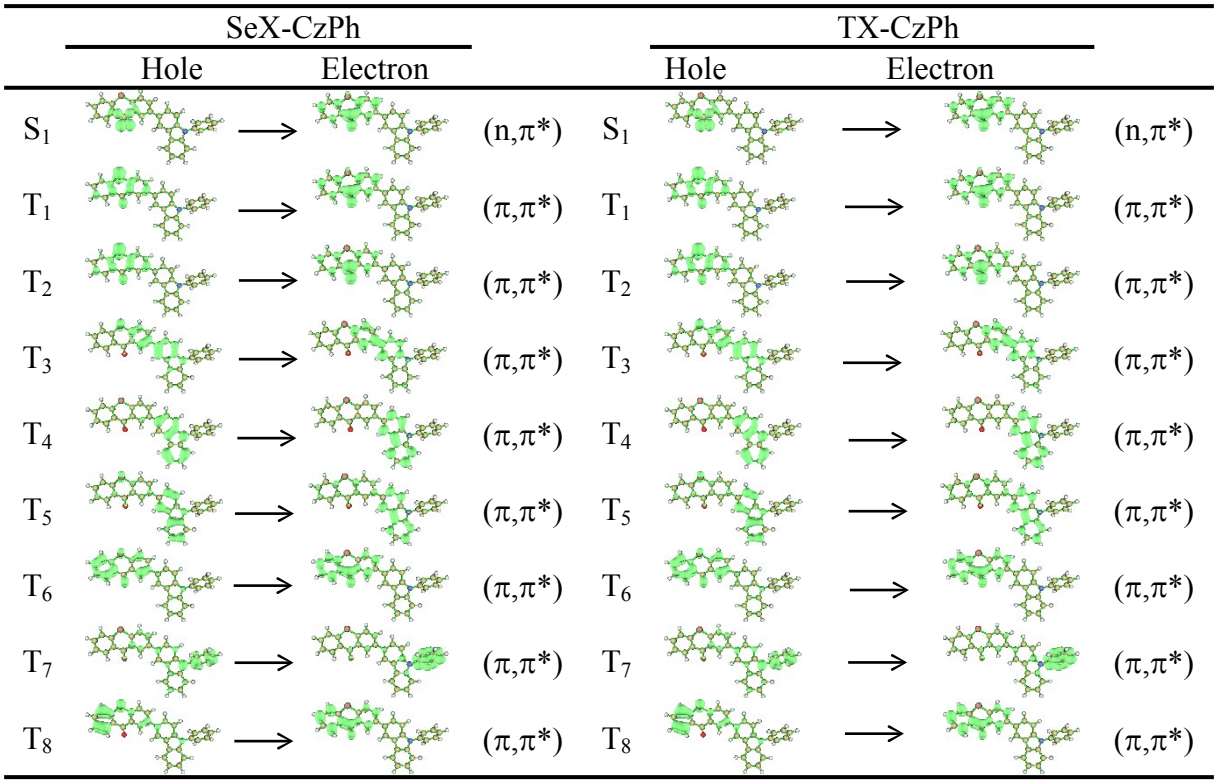


Figure S11. Hole-Electron analysis of SeX-CzPh and TX-CzPh in the lowest single (S_1) and triplet manifolds (Tn) base on the geometry of S_1 state.

Table S6. Energy levels of SeX-CzPh monomer

Excited state	Energy level (eV)
S_1	3.7451
T_1	3.0549
T_2	3.3635
T_3	3.4572
T_4	3.6218
T_5	3.7397
T_6	3.7758
T_7	4.0095
T_8	4.1093

Table S7. SOC constant of SeX-CzPh monomer

	SOC (cm^{-1})
$\zeta_{S0\text{-}T1}$	4.09
$\zeta_{S1\text{-}T1}$	52.50
$\zeta_{S1\text{-}T2}$	3.80
$\zeta_{S1\text{-}T3}$	13.00
$\zeta_{S1\text{-}T4}$	0.99
$\zeta_{S1\text{-}T5}$	8.48
$\zeta_{S1\text{-}T6}$	4.17
$\zeta_{S1\text{-}T7}$	2.02
$\zeta_{S1\text{-}T8}$	14.20

Table S8. Energy levels of TX-CzPh monomer

Excited state	Energy level (eV)
S_1	3.7819
T_1	3.1064
T_2	3.4025
T_3	3.4349
T_4	3.6208
T_5	3.7325
T_6	3.7957
T_7	4.0135
T_8	4.1332

Table S9. SOC constant of TX-CzPh monomer

	SOC (cm^{-1})
$\zeta_{S0\text{-}T1}$	1.33
$\zeta_{S1\text{-}T1}$	26.19
$\zeta_{S1\text{-}T2}$	2.02
$\zeta_{S1\text{-}T3}$	4.47
$\zeta_{S1\text{-}T4}$	2.23
$\zeta_{S1\text{-}T5}$	7.87
$\zeta_{S1\text{-}T6}$	11.01
$\zeta_{S1\text{-}T7}$	3.04
$\zeta_{S1\text{-}T8}$	9.78

Reference

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