Supplementary information

A Functional Unit Combination Strategy for Enhancing Red Room-Temperature Phosphorescence

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SI Materials and general methods

General information: All regents and solvents used for the synthesis were purchased commercially and without further purification. ¹H and ¹³C NMR spectra of the prepared compounds were recorded on a Bruker AVANCE 500 spectrometer using TMS as the internal standard and entire deuteration DMSO and CDCl₃ as solvents. Mass spectra were recorded using a Thermo Fisher ITQ1100 instrument. The compounds were characterized by a vario MICRO cube CHNS elemental analysis instrument by Elementar company.

Photophysical measurements: UV-vis absorption spectra of solutions were carried out on a Shimadzu UV-3100 Spectrophotometer. Photoluminescence (PL) spectra and time-resolved PL spectra of solutions, films, and crystals were recorded on a FLS980 Spectrofluorometer. Photoluminescence quantum yields (PLQY) of solutions, films, and crystals were measured using an integrating sphere apparatus on a FLS980 Spectrofluorometer under ambient condition. The phosphorescence quantum yield (Φ_P) can be calculated by area integral of phosphorescence and fluorescence emission bands of PL spectra under the same condition. PL spectra and time-resolved PL spectra of films in vacuum were collected on a FLSP980 Spectrofluorometer equipped with a chamber (Optistat DN2, OXFORD INSTRUMENTS) and a vacuum pump. The detailed data for thianthrene (TA), phenoxathiine (PX), and dibenzo[b,e][1,4]dioxine (DX) are presented by our previous work.^[1] In the experiment of investigating oxygen-sensitive properties, oxygen/nitrogen mixed gases with different oxygen concentrations were bought in the form of a standard gas from a company called Changchun Juyang Gas Co. LTD. Each standard gas was stored in a 10 L steel cylinder. PL spectra and time-resolved PL spectra of SS-BZT and SO-BZT at different oxygen concentrations were collected using a FLSP980 Spectrofluorometer equipped with a chamber (Optistat DN2, OXFORD INSTRUMENTS) and a vacuum pump. Firstly, the chamber was connected with the vacuum pump and steel cylinder through a three-port valve. Secondly, the chamber was vacuumed by the vacuum pump. Thirdly, the chamber was filled with gas, which was driven by negative pressure. A rubber ball connected to pipe was used to buffer the gas pressure, and thus the experimental environment was considered to be under atmosphere pressure. Oxygen partial pressure was estimated according to a product rule between volume percentage of oxygen in standard gas and atmosphere pressure. Before starting each experimental measurement, the gas with a certain oxygen concentration used for spectral collection in the chamber was displaced three times back and forth by pumping and inflating.

Theoretical calculation: Density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were worked out using B3LYP/6-31G (d, p) by Gaussian 09 (version D.01) package^[2] to optimize the geometries of the ground states and the lowest singlet states for these compounds, respectively. And the natural transition orbitals (NTOs)^[3] of S₁ and T_n (n = 1, 2) were calculated based on B3LYP/6-31G (d, p). The spin–orbit coupling (SOC) coefficients were quantitatively estimated using B3LYP/6-31G (d, p) by a Beijing density function (BDF) program.^[4]

Single crystal X-ray diffraction (SCXRD) data: Single crystals of SS-BZT, SO-BZT, and OO-BZT were grown by solvent evaporation of dichloromethane (DCM) and n-hexane (HEX) mixtures. BZT crystal was obtained by solvent diffusion of DCM and methanol mixtures, these samples were placed in a crystal incubator with constant temperature. The diffraction experiments were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo-K α and control Software using the RAPID AUTO at room temperature. The crystal structures were solved and refined using the Olex2 software.

SII Synthesis details



Scheme S1. Synthesis routes of 5,6-2F-BZT, SS-BZT, SO-BZT, and OO-BZT.

Benzo[c][1,2,5]thiadiazole (BZT) was purchased commercially and further purified via silica gel chromatography using DCM:petroleum ether = 1:3 as eluent to give a white needle crystal. ¹H NMR (500 MHz, DMSO-*d*₆, 25 °C, TMS): δ = 8.12 (m, 2H), 7.74 (m, J = 6.2, 3.1 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃, 25 °C, TMS): δ = 154.812 (C), 129.303 (CH), 121.565 (CH); GC-MS, EI, mass m/z: 136.42 [M+]. anal. calcd for C₆H₄N₂S: C 52.92, H 2.96, N 20.57, S 23.54; found: C 51.99, H 2.94, N 20.06, S 23.41.

Synthesis of 5,6-difluorobenzo[c][1,2,5]thiadiazole (5,6-2F-BZT)

4,5-difluorobenzene-1,2-diamine (20 mmol, 2.88 g) and triethylamine (Et₃N) (80 mmol, 12 ml) were added into 60 ml dry DCM under ice bath. A mixture of thionyl chloride (50 mmol, 3.8 ml) and 10 ml dry DCM was slowly dropped, stirred and refluxed at 60 °C for 5 h. After cooling to room temperature, the mixture was extracted with DCM, the solvent was removed in vacuum. The crude product was purified via silica gel chromatography using DCM:petroleum ether = 1:1 (v:v) as eluent to give a white powder 5,6-2F-BZT with a yield of 86.6% (2.98 g). ¹H NMR (500 MHz, DMSO-*d*₆, 25 °C, TMS): δ = 8.29 (t, J = 9.3 Hz, 2H). GC-MS, EI, mass m/z: 172.20 [M+].

Synthesis of thianthreno[2,3-*c*][1,2,5]thiadiazole (SS-BZT)

A mixture of 5,6-2F-BZT (5 mmol, 0.86 g), benzene-1,2-dithiol (5 mmol, 0.71 g), K₂CO₃ (15 mmol, 2.07 g) and 12 ml *N*,*N*-Dimethylformamide (DMF) was degassed and recharged under nitrogen atmosphere. Then stirred and heated at 80 °C for 16 h. After cooling to room temperature, the mixture was poured into distilled water and hydrochloric acid was added to adjust PH to 7. The residue was filtered and the solvent was removed in vacuum. The crude product was purified via silica gel chromatography using DCM:petroleum ether = 1:3 (v:v) as eluent to give a yellow needle crystal with a yield of 89.8% (1.23 g). ¹H NMR (500 MHz, DMSO-*d*₆, 25 °C, TMS): δ = 8.39 (s, J = 0.9 Hz, 2H), 7.68 (dd, J = 5.8, 3.4 Hz, 2H), 7.43 (dd, J = 5.8, 3.3 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃, 25 °C, TMS): δ = 154.162 (C), 138.847 (C), 134.211 (C), 129.006 (CH), 128.255 (CH), 119.091 (CH); GC-MS, EI, mass m/z: 274.15 [M+]. anal. calcd for C₁₂H₆N₂S₃: C 52.53, H 2.20, N 10.21, S 35.05; found: C 53.08, H 2.28, N 10.30, S 35.12.

Synthesis of phenoxathiino[2,3-c][1,2,5]thiadiazole (SO-BZT):

A mixture of 5,6-2F-BZT (10 mmol, 1.72 g), 2-mercaptophenol (10 mmol, 1.26 g), K₂CO₃ (30 mmol, 4.14 g) and 12 ml DMF was degassed and recharged under nitrogen atmosphere. Then stirred and heated at 80 °C for 16 h. After cooling to room temperature, the mixture was poured into distilled water and added hydrochloric acid to adjust PH to 7. The residue was filtered and the solvent was removed in vacuum. The crude product was purified via silica gel chromatography using DCM:petroleum ether = 1:3 as eluent to give a yellow powder (1.78 g, 69.0%).¹H NMR (500 MHz, DMSO-d6, 25 °C, TMS): δ = 8.16 (s, 1H), 7.77 (s, 1H), 7.42 (dd, J=7.7, 1.5 Hz, 1H), 7.32 (td, J=7.7, 7.3, 1.6 Hz, 1H), 7.25 (dd, J=8.2, 1.4 Hz, 1H), 7.20 (td, J=7.5, 1.4 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃, 25 °C, TMS): δ = 154.589 (C), 153.055 (C), 152.198 (C), 150.497 (C), 127.914 (C), 117.821 (C), 128.190 (CH), 126.599 (CH), 124.886 (CH), 118.189 (CH), 116.413 (CH), 105.899 (CH); GC-MS, EI, mass m/z: 258.22 [M+].

Synthesis of benzo[5',6'][1,4]dioxino[2',3':4,5]benzo[1,2-c][1,2,5]thiadiazole (OO-BZT)

A mixture of 5,6-2F-BZT (10 mmol, 1.72 g), pyrocatechol (10 mmol, 1.10 g), K₂CO₃ (30 mmol,

4.14 g) and 12 ml DMF was degassed and recharged under nitrogen atmosphere. Then stirred and heated at 80 °C for 16 h. After cooling to room temperature, the mixture was poured into distilled water and added hydrochloric acid to adjust PH to 7. The residue was filtered and the solvent was removed in vacuum. The crude product was purified via silica gel chromatography using DCM:petroleum ether = 1:3 as eluent to give a light yellow solid (1.69 g, 69.8%). ¹H NMR (500 MHz, DMSO-*d*₆, 25 °C, TMS): δ = 7.67 (s, 2H), 7.18 (s, 2H), 7.11 (s, 2H); ¹³C NMR (126 MHz, CDCl₃, 25 °C, TMS): δ = 152.123 (C), 145.941 (C), 140.278 (C), 124.398 (CH), 116.618 (CH), 104.167 (CH); GC-MS, EI, mass m/z: 242.18 [M+].

SIII Figures and tables



Figure S1. Molecular design, molecular structures, and optimized geometries based on ground state (S₀) of BZT, SS-BZT, SO-BZT, and OO-BZT.



Photophysical properties and packing structures of crystals

Figure S2. PL spectra of (a) SS-BZT, (b) TA, and (c) BZT crystals at RT. (d) Single crystal structures and molecular stacking models of SS-BZT, TA, and BZT (from left to right).

The directions of transition dipoles are along the long axis for SS-BZT, SO-BZT, and OO-BZT, but along the short axis for BZT. The angles between molecular transition dipole and its slippage in the crystals are 85.64°, 75.28°, 76.66°, and 77.86° for BZT, SS-BZT, SO-BZT, and OO-BZT, respectively, which are larger than 54.7°, defined as the critical angle, indicating H-aggregation type for these molecules in crystals.^[5-7] H-aggregation type in crystals is generally regarded as a condition adverse to PL properties, which is consistent with experimental results. For example, the PLQYs of SS-BZT in THF solution and crystal are 1.46% and 0.50%. In addition, the PLQYs of diluted in THF solution and crystal are estimated as 3.00% and 0.51% for SO-BZT, 26.92% and 3.91% for OO-BZT, respectively. The above experiment results further verify the influence of H-aggregation in the crystals for PL properties.



Figure S3. Single crystal structures and molecular stacking models of SO-BZT (left) and OO-BZT (right).



Figure S4. Single crystal structures and molecular stacking models of PX (left) and DX (right).



Figure S5. PL spectra of (a) SS-BZT, (b) SO-BZT, (c) OO-BZT, and (d) BZT crystals at RT and 77 K. Insets are luminescence images of the crystals recorded at RT.



Figure S6. (a)(b) Time-resolved PL spectra of SS-BZT, SO-BZT, OO-BZT, and BZT crystals at RT; (c)(d) Time-resolved PL spectra of SS-BZT, SO-BZT, OO-BZT, and BZT crystals at 77 K.



Figure S7. PL spectra and luminescence images of (a) TA, (b) PX, and (c) DX crystals at RT. Timeresolved PL spectra of (d) TA, (e) PX, and (f) DX crystals at RT.



Figure S8. Images of different doping ratios SO-BZT:BPO, OO-BZT:BPO, and BZT:BPO doped crystals under sunlight and UV (365 nm) irradiation.



Figure S9. (a) Normalized PL spectra of SO-BZT:BPO doped crystals. (b)(c) Time-resolved PL spectra of SO-BZT:BPO doped crystals (monitored at 447 nm and 610 nm).



Figure S10. (a) Normalized PL spectra of OO-BZT:BPO doped crystals. (b)(c) Time-resolved PL spectra of OO-BZT:BPO doped crystals (monitored at 447 nm and 590 nm).



Figure S11. (a) Normalized PL spectra of BZT:BPO doped crystals. (b)(c) Time-resolved PL spectra of BZT:BPO doped crystals (monitored at 447 nm and 600 nm).

Doped crystals	0.01 wt.%	0.05 wt.%	0.10 wt.%	0.20 wt.%	0.50 wt.%	1.00 wt.%
	${oldsymbol{\varPhi}}_{ m P}/ au_{ m P}$	${oldsymbol{\varPhi}}_{ m P}/ au_{ m P}$	$oldsymbol{\Phi}_{ m P}/ au_{ m P}$	$oldsymbol{\Phi}_{ m P}/ au_{ m P}$	$oldsymbol{\Phi}_{ m P}/ au_{ m P}$	$oldsymbol{\Phi}_{ ext{P}}/ au_{ ext{P}}$
SS-BZT:BPO	0.21%/	0.60%/	2.33%/	1.44%/	1.42%/	1.64%/
	14.12 ms	13.82 ms	14.32 ms	14.13 ms	14.08 ms	14.08 ms
SO-BZT:BPO	0.27%/	0.35%/	1.57%/	1.92%/	1.91%/	2.15%/
	18.83 ms	15.85 ms	19.04 ms	18.97 ms	18.94 ms	18.90 ms
OO-BZT:BPO	0.24%/	0.16%/	0.46%/	0.67%/	0.64%/	1.19%/
	26.39 ms	26.03 ms	34.27 ms	34.45 ms	34.66 ms	34.63 ms
BZT:BPO	0.12%/	0.22%/	0.16%/	0.10%/	0.20%/	0.38%/
	18.31 ms	17.89 ms	19.77 ms	20.02 ms	19.57 ms	19.06 ms

Table S1. Phosphorescence quantum yields (Φ_{PS}) and phosphorescence lifetimes (τ_{PS}) of SS-BZT:BPO, SO-BZT:BPO, OO-BZT:BPO, and BZT:BPO doped crystals with different doping ratios.

Photophysical properties of monomolecular solution



Figure S12. UV-vis absorption spectra of (a) SS-BZT, (b) TA, and (c) BZT dispersed in hexane (HEX), diethyl ether (ETE), tetrahydrofuran (THF), and acetonitrile (ACN) at 10^{-5} mol·L⁻¹. (d) UV-vis absorption spectra of SS-BZT, TA, and BZT dispersed in THF solution at 10^{-5} mol·L⁻¹.



Figure S13. UV-vis absorption spectra of (a) SO-BZT, (b) OO-BZT, (c) PX, and (d) DX dispersed in HEX, ETE, THF, and ACN at 10⁻⁵ mol·L⁻¹.



Figure S14. PL spectra of (a) SS-BZT, (b) TA, and (c) BZT dispersed in HEX, ETE, THF, and ACN at 10⁻⁵ mol·L⁻¹. (d) PL spectra of SS-BZT, TA, and BZT dispersed in THF solution at 10⁻⁵ mol·L⁻¹.



Figure S15. PL spectra of (a) SO-BZT, (b) OO-BZT, (c) PX, and (d) DX dispersed in HEX, ETE, THF, and ACN at 10⁻⁵ mol·L⁻¹.



Figure S16. NTOs observed from different views of S_1 state based on optimized geometries of excited singlet state for (a) SS-BZT and (b) SO-BZT (isoval=0.05).



Figure S17. NTOs observed from different views of S_1 state based on optimized geometries of excited singlet state for (a) OO-BZT and (b) BZT (isoval=0.05).



Figure S18. PL spectra (condition: RT and 77 K), gated PL spectra (delay time: 1 ms) and luminescence images (excited source: on and off) of (a) SO-BZT, (b) OO-BZT, (c) PX, and (d) DX dispersed in THF solution at 10⁻⁵ mol·L⁻¹.



Figure S19. Time-resolved PL spectra monitored at fluorescence bands of (a)(b) SS-BZT and (d)(e) BZT dispersed in THF solution $(10^{-5} \text{ mol} \cdot \text{L}^{-1})$ at RT and 77 K. (c) Time-resolved PL spectra monitored at fluorescence band of TA dispersed in THF solution $(10^{-5} \text{ mol} \cdot \text{L}^{-1})$ at RT. (f) Time-resolved PL spectra monitored at phosphorescence bands of SS-BZT, TA, and BZT dispersed in THF solution $(10^{-5} \text{ mol} \cdot \text{L}^{-1})$ at 77 K.



Figure S20. Time-resolved PL spectra recorded at fluorescence bands of (a)(b) SO-BZT and (d)(e) OO-BZT dispersed in THF solution $(10^{-5} \text{ mol}\cdot\text{L}^{-1})$ at RT and 77 K. Time-resolved PL spectra recorded at phosphorescence bands of (c) SO-BZT and (f) OO-BZT dispersed in THF solution $(10^{-5} \text{ mol}\cdot\text{L}^{-1})$ at 77 K.



Figure S21. Time-resolved PL spectra recorded at fluorescence and phosphorescence bands of (a)(b) PX and (c)(d) DX dispersed in THF solution $(10^{-5} \text{ mol} \cdot \text{L}^{-1})$ at RT and 77 K.

	λ_{F}	$ au_{ m F}$	λ' _F	$ au'_{ m F}$	λp	$ au'_{ m P}$	PLQY
	(nm)	(ns)	(nm)	(ns)	(nm)	(ms)	(%)
SS-BZT	515	/	470	0.60(100%)	620	22.16	1.46
						[17.07(27.59%)	
						23.57(72.41%)]	
ТА	436	8.31	420	/	486	55.39	1.53
						[25.08(19.28%)	
						58.49(80.72%)]	
BZT	384	/	380	/	600	32.10	0.51
						[19.97(17.61%)	
						33.64(82.39%)]	
SO-BZT	480	/	460	0.68(100%)	610	25.99	3
						[18.38(12.45%)	
						26.73(87.55)]	
РХ	375	8.92	/	/	439	99.44	/
						[24.46(5.49%)	
						100.50(94.51%)]	
					463	100.09	
						[30.15(5.91%)	
						101.40(94.09%)]	
OO-BZT	442	18.17	420	10.32	600	47.81(100%)	19.46
		[1.968(97.78%)		[2.77(98.27%)			
		47.65(2.22%)]		40.00(1.73%)]			
DX	364	6.79	/	/	403	906.7(100%)	/
					422	793.7(100%)	

Table S2. Photophysical data of SS-BZT, TA, BZT, SO-BZT, PX, OO-BZT, and DX diluted in THF solution at 10⁻⁵ mol·L⁻¹.

Here, λ_F and τ_F represent fluorescence emission bands and their lifetimes monitored at fluorescence emission bands at RT; λ'_F and λ'_P represent their fluorescence and phosphorescence emission bands at 77 K; τ'_F and τ'_P represent their lifetimes recorded at fluorescence and phosphorescence emission bands at 77 K, respectively; PLQYs were recorded at RT.

Photophysical properties of doped films



Figure S22. PL spectra of 1.00 wt.% doped PMMA films for (a) SS-BZT, (b) SO-BZT, (c) OO-BZT, and (d) BZT at RT (in air and vacuum) and 77 K. PL spectra of 1.00 wt.% doped PMMA films for (e) PX and (f) DX at RT (in air and vacuum).



Figure S23. (a)(b) Time-resolved PL spectra of 1.00 wt.% doped PMMA films for SO-BZT and OO-BZT at RT (in air and vacuum). (c)(d) Time-resolved PL spectra of 1.00 wt.% doped PMMA films for SS-BZT, SO-BZT, OO-BZT, and BZT at 77 K.



Figure S24. Time-resolved PL spectra of 1.00 wt.% doped PMMA films for (a)(b) PX and (c) DX at RT (in air and vacuum).

Compound	τf	${\pmb \Phi}_{ m F}$	$ au_{ m P}$	${\pmb \phi}_{ m P}$	k _r F	k _{nr} F	k ^P	k _{nr} ^P	kısc
	(ns)	(%)	(ms)	(%)	(s ⁻¹)	(s ⁻¹)	(s ⁻¹)	(s ⁻¹)	(s ⁻¹)
SS-BZT	1.76	2.67	10.70	1.73	1.5×10 ⁷	5.4×10 ⁸	1.6	9.2×10 ¹	9.8×10 ⁶ -5.5×10 ⁸
ТА	11.41	3.60	23.36	31.3	3.2×10 ⁶	5.7×10 ⁷	1.3×10 ¹	2.9×10 ¹	2.7×10 ⁷ -8.4×10 ⁷
BZT	3.13	0.43	14.17	0.13	1.4×10 ⁶	3.2×10 ⁸	9.2×10 ⁻²	7.0×10 ¹	4.2×10 ⁵ -3.2×10 ⁸
SO-BZT	1.73	3.00	13.05	1.02	1.7×10 ⁷	5.5×10 ⁸	7.8×10 ⁻¹	7.6×10 ¹	5.9×10 ⁶ -5.6×10 ⁸
РХ	11.65	0.20	9.85	1.20	1.7×10 ⁵	8.5×10 ⁷	1.2	1.0×10 ²	1.0×10 ⁶ -8.6×10 ⁷
OO-BZT	2.37	19.46	18.76	0.16	8.2×10 ⁷	3.4×10 ⁸	8.5×10 ⁻²	5.3×10 ¹	6.8×10 ⁵ -3.4×10 ⁸
DX	1.58	0.60	/	/	3.8×10 ⁶	6.3×10 ⁸	/	/	/

Table S3. Photophysical parameters of 1.00 wt.% doped PMMA films for SS-BZT, TA, BZT, SO-BZT, PX, OO-BZT, and DX at RT.

Here, k_r^F and k_{nr}^F , k_r^P and k_{nr}^P represent the rates for radiation and non-radiation process for fluorescence and phosphorescence, respectively. k_{ISC} represents the transition rates for ISC process. $k_r^F = \Phi_F / \tau_F$; $k_{nr}^F = (1 - \Phi_F - \Phi_P) / \tau_F$; $k_r^P = \Phi_P / \tau_P$; $k_{nr}^P = (1 - \Phi_P) / \tau_P$; $k_{ISC}^{\min} = \Phi_P / \tau_F \le k_{ISC} \le (1 - \Phi_F) / \tau_F = k_{ISC}^{\max}$.^[8]

Theoretical calculation



Figure S25. NTOs observed from different views of T_1 state based on optimized geometries of excited singlet state for (a) SS-BZT and (b) SO-BZT (isoval=0.05).



Figure S26. NTOs observed from different views of T_2 state based on optimized geometries of excited singlet state for (a) SS-BZT and (b) SO-BZT (isoval=0.05).



Figure S27. NTOs observed from different views of T_1 state based on optimized geometries of excited singlet state for (a) OO-BZT and (b) BZT (isoval=0.05).



Figure S28. NTOs observed from different views of T_2 state based on optimized geometries of excited singlet state for (a) OO-BZT and (b) BZT (isoval=0.05).



Figure S29. Energy level diagram based on optimized geometries of excited singlet state of SS-BZT, SO-BZT, OO-BZT, and BZT.

	SS-BZT	SO-BZT	OO-BZT	BZT
ζ(S ₀ -T ₁)	3.433	3.552	0.126	0.589
ζ(S ₁ -T ₁)	4.956	3.241	0.264	0.001
ζ(S ₁ -T ₂)	3.377	2.111	0.000	1.305
ζ(S1-T3)	3.988	4.469	0.154	7.288
ζ(S ₁ -T ₄)	9.145	6.356	20.811	0.006
ζ(S ₁ -T ₅)	2.204	18.584	0.063	12.308
ζ(S ₂ -T ₁)	1.389	0.722	0.001	1.100
$\zeta(S_2-T_2)$	0.539	2.542	0.333	36.933
ζ(S2-T ₃)	1.855	0.538	0.000	0.008
ζ(S2-T4)	2.384	1.704	5.929	0.440
$\zeta(S_2-T_5)$	3.550	6.230	1.313	12.140
ζ(S ₃ -T ₁)	3.800	2.707	0.001	2.312
ζ(S ₃ -T ₂)	3.874	4.642	0.027	0.008
ζ(S ₃ -T ₃)	1.645	2.141	0.000	38.084
ζ(S3-T4)	3.575	2.753	4.053	0.115
ζ(S ₃ -T ₅)	3.832	4.531	0.187	38.954

Table S4. SOC coefficients of S_n - T_m (n=0,1,2,3; m=1,2,3,4,5) at optimized geometries of ground state for SS-BZT, SO-BZT, OO-BZT, and BZT.

	SS-BZT	SO-BZT	OO-BZT	BZT
ζ(S ₀ -T ₁)	1.052	0.963	0.014	0.358
ζ(S ₁ -T ₁)	3.366	1.708	0.063	0.000
ζ(S ₁ -T ₂)	2.050	1.673	0.000	1.207
ζ(S1-T3)	2.065	2.316	0.025	8.014
ζ(S ₁ -T ₄)	7.766	5.766	0.001	0.000
ζ(S ₁ -T ₅)	0.969	2.424	0.486	11.893
$\zeta(S_2-T_1)$	0.622	1.090	0.000	0.374
ζ(S ₂ -T ₂)	1.240	2.098	0.086	40.711
ζ(S ₂ -T ₃)	1.166	0.379	0.000	0.001
ζ(S ₂ -T ₄)	1.910	0.916	1.270	1.185
ζ(S ₂ -T ₅)	1.471	0.438	0.001	19.553
ζ(S ₃ -T ₁)	1.818	1.432	0.000	2.153
ζ(S ₃ -T ₂)	2.764	1.107	0.215	0.001
ζ(S3-T3)	1.021	0.399	0.000	43.208
ζ(S3-T4)	1.319	0.897	0.407	0.030
ζ(S ₃ -T ₅)	1.679	0.401	0.001	49.137

Table S5. SOC coefficients of S_n - T_m (n=0,1,2,3; m=1,2,3,4,5) at optimized geometries of excited singlet state for SS-BZT, SO-BZT, OO-BZT, and BZT.



Figure S30. Molecular configurations of SS-BZT, SO-BZT, OO-BZT, and BZT based on optimized geometries of S₀ and S₁ states along top and front views.


Figure S31. The SOC coefficients of S_1 - T_1 based on molecular geometries for (a) SS-BZT, (b) SO-BZT, and (c) OO-BZT crystals in different folding angles. (d) The SOC coefficients of S_1 - T_1 based on molecular geometries for SS-BZT, SO-BZT, and OO-BZT crystals.



Figure S32. The SOC coefficients of S_1 - T_2 based on molecular geometries for (a) SS-BZT, (b) SO-BZT, and (c) OO-BZT crystals in different folding angles. (d) The SOC coefficients of S_1 - T_2 based on molecular geometries for SS-BZT, SO-BZT, and OO-BZT crystals.

Compared with BZT, SS-BZT and SO-BZT show increased SOC coefficients between S₁ to T_n (n=1, 2), meaning improved ISC process for SS-BZT and SO-BZT. Hereinto, SOC coefficients of S₀-T₁, S₁-T₁ and S₁-T₂ successively decrease from SS-BZT, SO-BZT to OO-BZT, which can be attributed to enhanced SOC originated from the smallest folding angle for SS-BZT and non-bonding electrons of sulfur atoms participating in orbital transition process. While OO-BZT shows destructive SOC between S₁ to T₂ accompanied with very small SOC coefficients for ISC (S₁-T₁ and S₁-T₂) process and phosphorescence radiation (T₁-S₀), resulting in the weakest RTP (Tables S4 and S5). From BZT to SS-BZT and SO-BZT, the transition characters of the S₁ and T_n (n=1, 2) are changed from (π , π^*) to the mixing of (n, π^*) and (π , π^*), which indicates that the n electrons of S atoms participate in the transition process (Figures S16, S17, and S25-S28). However, OO-BZT shows a (π , π^*) transition configuration for the S₁ and T_n (n=1, 2) state. According to El-Sayed rule, it is contributed to accelerating ISC process that different electronic configuration for orbital transition, that is why SS-BZT and SO-BZT show efficient red RTP but OO-BZT with weak RTP characteristic.

	SS-BZT	SO-BZT	OO-BZT
100°	6.544	8.727	2.559
110°	9.019	9.386	2.135
120°	7.285	7.287	3.020
130°	5.661	5.478	2.760
140°	4.539	4.097	2.266
150°	3.671	3.006	1.761
160°	2.903	2.046	1.264
170°	0.334	1.149	0.769
180°	0.171	0.425	0.392

Table S6. The SOC coefficients of S_1 - T_1 based on molecular geometries for SS-BZT, SO-BZT, and OO-BZT crystals in different folding angles θ (100°-180°).

NTOs of S₁ and T₁ for SS-BZT, SO-BZT, and OO-BZT crystals in different folding angles θ (100-180°) are shown in Figures S33-S59 (isoval = 0.05).



Figure S33. NTOs of S_1 and T_1 based on folded configurations of SS-BZT crystal at a θ of 100°.



Figure S34. NTOs of S_1 and T_1 based on folded configurations of SS-BZT crystal at a θ of 110°.



Figure S35. NTOs of S_1 and T_1 based on folded configurations of SS-BZT crystal at a θ of 120°.



Figure S36. NTOs of S_1 and T_1 based on folded configurations of SS-BZT crystal at a θ of 130°.



Figure S37. NTOs of S_1 and T_1 based on folded configurations of SS-BZT crystal at a θ of 140°.



Figure S38. NTOs of S_1 and T_1 based on folded configurations of SS-BZT crystal at a θ of 150°.



Figure S39. NTOs of S_1 and T_1 based on folded configurations of SS-BZT crystal at a θ of 160°.



Figure S40. NTOs of S_1 and T_1 based on folded configurations of SS-BZT crystal at a θ of 170°.



Figure S41. NTOs of S_1 and T_1 based on folded configurations of SS-BZT crystal at a θ of 180°.



Figure S42. NTOs of S_1 and T_1 based on folded configurations of SO-BZT crystal at a θ of 100°.



Figure S43. NTOs of S_1 and T_1 based on folded configurations of SO-BZT crystal at a θ of 110°.



Figure S44. NTOs of S_1 and T_1 based on folded configurations of SO-BZT crystal at a θ of 120°.



Figure S45. NTOs of S_1 and T_1 based on folded configurations of SO-BZT crystal at a θ of 130°.



Figure S46. NTOs of S_1 and T_1 based on folded configurations of SO-BZT crystal at a θ of 140°.



Figure S47. NTOs of S_1 and T_1 based on folded configurations of SO-BZT crystal at a θ of 150°.



Figure S48. NTOs of S_1 and T_1 based on folded configurations of SO-BZT crystal at a θ of 160°.



Figure S49. NTOs of S_1 and T_1 based on folded configurations of SO-BZT crystal at a θ of 170°.



Figure S50. NTOs of S_1 and T_1 based on folded configurations of SO-BZT crystal at a θ of 180°.



Figure S51. NTOs of S_1 and T_1 based on folded configurations of OO-BZT crystal at a θ of 100°.



Figure S52. NTOs of S_1 and T_1 based on folded configurations of OO-BZT crystal at a θ of 110°.



Figure S53. NTOs of S_1 and T_1 based on folded configurations of OO-BZT crystal at a θ of 120°.



Figure S54. NTOs of S_1 and T_1 based on folded configurations of OO-BZT crystal at a θ of 130°.



Figure S55. NTOs of S_1 and T_1 based on folded configurations of OO-BZT crystal at a θ of 140°.



Figure S56. NTOs of S_1 and T_1 based on folded configurations of OO-BZT crystal at a θ of 150°.



Figure S57. NTOs of S_1 and T_1 based on folded configurations of OO-BZT crystal at a θ of 160°.



Figure S58. NTOs of S_1 and T_1 based on folded configurations of OO-BZT crystal at a θ of 170°.



Figure S59. NTOs of S_1 and T_1 based on folded configurations of OO-BZT crystal at a θ of 180°.





Figure S60. PL spectra of (a) SS-BZT, (b) SO-BZT, (c) OO-BZT, and (d) BZT crystals at RT (in air and vacuum).



Figure S61. PL spectra of 0.10 wt.% SS-BZT:BPO doped crystal at RT (in air and vacuum).



Figure S62. Normalized absorption spectra of 1.00 wt.% (a) SS-BZT and (B) SO-BZT doped PMMA and Zeonex films.



Figure S63. (a) PL spectra and (b) plot of I_0/I against $[O_2]$ for 1.00 wt.% SS-BZT doped PMMA film in different $[O_2]$. (c) Time-resolved PL spectra and (d) plot of τ_0/τ against $[O_2]$ for 1.00 wt.% SS-BZT doped PMMA film in different $[O_2]$. (e) The Commission Internationale del'Eclairage (CIE) coordinates of SS-BZT doped PMMA film with decreasing $[O_2]$. (f) Images of SS-BZT doped PMMA film under 365 nm irradiation with decreasing $[O_2]$.



Figure S64. (a) PL spectra and (b) plot of I_0/I against $[O_2]$ for 1.00 wt.% SO-BZT doped PMMA film in different $[O_2]$. (c) Time-resolved PL spectra and (d) plot of τ_0/τ against $[O_2]$ for 1.00 wt.% SO-BZT doped PMMA film in different $[O_2]$. (e) The CIE coordinates of SO-BZT doped PMMA film with decreasing $[O_2]$. (f) Images of SO-BZT doped PMMA film under 365 nm irradiation with decreasing $[O_2]$.



Figure S65. PL spectra of 1.00 wt.% (a) SS-BZT and (b) SO-BZT doped PMMA films ($[O_2]$ =0.90%). Time-resolved PL spectra of 1.00 wt.% (c) SS-BZT and (d) SO-BZT doped PMMA films monitored at phosphorescence bands, respectively ($[O_2]$ =0.90%).



Figure S66. Spectral reversibility and reproducibility of (a) SS-BZT and (b) SO-BZT in doped PMMA films.



Figure S67. (a) PL spectra and (b) plot of I_0/I against $[O_2]$ of 1.00 wt.% SS-BZT doped Zeonex film in different $[O_2]$. (c) Time-resolved PL spectra and (d) plot of τ_0/τ against $[O_2]$ of 1.00 wt.% SS-BZT doped Zeonex film in different $[O_2]$. (e) The CIE coordinates of SS-BZT doped Zeonex film with decreasing $[O_2]$.



Figure S68. (a) PL spectra and (b) plot of I_0/I against $[O_2]$ of 1.00 wt.% SO-BZT doped Zeonex film in different $[O_2]$. (c) Time-resolved PL spectra and (d) plot of τ_0/τ against $[O_2]$ of 1.00 wt.% SO-BZT doped Zeonex film in different $[O_2]$. (e) The CIE coordinates of SO-BZT doped Zeonex film with decreasing $[O_2]$.

Compound	$K_{ m SV,\ intensity}$	$K_{ m SV,\ lifetime}$	$K_{ m SV,\ intensity}$	$K_{ m SV,\ lifetime}$
	(KPa ⁻¹) ^a	(KPa ⁻¹) ^a	(KPa ⁻¹) ^b	(KPa ⁻¹) ^b
SS-BZT	2.66	1.97	17.54	7.09
SO-BZT	3.63	2.11	26.35	9.49

Table S7. Experimental results of SS-BZT and SO-BZT doped films for oxygen detection.

^a $K_{SV, intensity}$ and $K_{SV, lifetime}$ are estimated by changed [O₂] for doped PMMA films.

 ${}^{b}K_{SV, intensity}$ and $K_{SV, lifetime}$ are estimated by changed [O₂] for doped Zeonex films.

¹H NMR and ¹³C NMR data



Figure S69 ¹H NMR spectra of 5,6-2F-BZT compound.



Figure S70¹H NMR spectra of SS-BZT compound.



Figure S71 ¹H NMR spectra of SO-BZT compound.



Figure S72 ¹H NMR spectra of OO-BZT compound.



Figure S73 ¹H NMR spectra of BZT compound.



Figure S74 ¹³C NMR spectra of SS-BZT compound.



Figure S75 ¹³C NMR spectra of SO-BZT compound.



Figure S76 ¹³C NMR spectra of OO-BZT compound.



Figure S77 ¹³C NMR spectra of BZT compound.

Crystallographic data

Compound	SS-BZT	SO-BZT	OO-BZT
crystal color	yellow	yellow	colorless
empirical formula	$C_{12}H_6N_2S_3$	$C_{12}H_6N_2OS_2$	$C_{12}H_6N_2O_2S$
formula weight	274.37	258.31	242.25
<i>T</i> [K]	293 K	293 K	293 K
crystal system	triclinic	monoclinic	monoclinic
space group	P -1	$P2_1/n$	C2/c
<i>a</i> [Å]	3.98040(10)	14.4489(10)	22.528(3)
<i>b</i> [Å]	11.8021(4)	3.8802(2)	3.9061(4)
<i>c</i> [Å]	12.6373(4)	18.6217(13)	22.895(3)
α [°]	103.6610(10)	90	90
β [°]	96.0630(10)	93.458(3)	96.977(10)
γ [°]	98.3570(10)	90	90
V [Å ³]	564.66(3)	1421.12(12)	1999.8(4)
Z	2	4	8
F(000)	280.0	528.0	992.0
density [g·cm⁻³]	1.614	1.646	1.609
μ [mm ⁻¹]	0.629	0.490	0.311
Reflections collected	23770	21421	32302
unique reflections	2572	2368	2279
<i>R</i> (int)	0.0247	0.0667	0.1074
GOF	1.098	1.035	1.098
$R_1 [I > 2\sigma(I)]$	0.0305	0.0414	0.0836
$\omega R_2 [I > 2\sigma(I)]$	0.0788	0.0920	0.2054
R_1 (all data)	0.0320	0.0651	0.1256
ωR_2 (all data)	0.0805	0.1034	0.2194
CCDC number	2266086	2266087	2266088

 Table S8. Crystallographic data for SS-BZT, SO-BZT, and OO-BZT.

H11 H12 H6 11 G12 G6 $C1$ H1 $C12$ $C6$ $C1$ $C1$ $C12$ $C6$ $C2$ $N2$ $C2$ $N2$ $H9$ $H3$ $H3$ $H3$ $H3$ $H3$ $H3$ $H3$ $H3$							
Atom	Atom	Length/Å	Atom	Atom	Length/Å		
S 1	N1	1.6172(15)	C2	C3	1.415(2)		
S 1	N2	1.6130(15)	C4	C3	1.3695(19)		
S2	C5	1.7628(14)	C5	C4	1.4366(18)		
S2	C7	1.7628(14)	C5	C6	1.369(2)		
S3	C4	1.7598(14)	C7	C12	1.394(2)		
S3	C8	1.7587(14)	C8	C7	1.3890(19)		
N1	C1	1.3522(19)	C8	С9	1.395(2)		
N2	C2	1.3480(19)	С9	C10	1.381(2)		
C1	C2	1.429(2)	C11	C10	1.381(3)		
C1	C6	1.415(2)	C12	C11	1.386(2)		

Table S9. Bond lengths (Å) for SS-BZT in the crystal.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	S 1	N1	101.24(7)	C4	C5	S2	120.28(10)
C7	S 2	C5	102.58(6)	C6	C5	S2	118.21(10)
C8	S 3	C4	102.56(6)	C6	C5	C4	121.36(12)
C1	N1	S 1	106.06(11)	C5	C6	C1	118.22(13)
C2	N2	S 1	106.13(11)	C8	C7	S2	120.91(10)
N1	C1	C2	113.09(14)	C8	C7	C12	119.97(13)
N1	C1	C6	126.40(14)	C12	C7	S2	119.07(11)
C6	C1	C2	120.50(13)	C7	C8	S 3	121.77(10)
N2	C2	C1	113.48(14)	C7	C8	C9	119.86(13)
N2	C2	C3	126.31(14)	C9	C8	S 3	118.34(11)
C3	C2	C1	120.20(13)	C10	C9	C8	119.70(15)
C4	C3	C2	118.40(13)	C11	C10	C9	120.55(15)
C3	C4	S 3	118.07(10)	C10	C11	C12	120.20(15)
C3	C4	C5	121.25(12)	C11	C12	C7	119.69(15)
C5	C4	S 3	120.57(10)				

 Table S10. Bond Angles for SS-BZT in the crystal.

$\begin{array}{c} H9 \\ H10 \\ C40 \\ H411 \\ H411 \\ C42 \\ H12 \\ H6 \end{array}$						
Atom	Atom	Length/Å	Atom	Atom	Length/Å	
S2	C8	1.752(2)	C5	C4	1.441(3)	
S2	C4	1.752(2)	C5	C6	1.355(3)	
S1	N1	1.621(2)	C2	C1	1.433(3)	
S1	N2	1.617(2)	C8	C7	1.384(3)	
O1	C5	1.371(3)	C8	С9	1.396(3)	
O1	C7	1.383(3)	C1	C6	1.417(3)	
N1	C1	1.344(3)	C7	C12	1.378(3)	
N2	C2	1.343(3)	С9	C10	1.377(3)	
C3	C2	1.411(3)	C12	C11	1.381(3)	
C3	C4	1.365(3)	C10	C11	1.377(4)	

Table S11. Bond lengths (Å) for SO-BZT in the crystal.
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	S2	C4	102.06(10)	N1	C1	C2	113.2(2)
N2	S 1	N1	100.83(10)	N1	C1	C6	126.7(2)
C5	01	C7	124.02(17)	C6	C1	C2	120.1(2)
C1	N1	S 1	106.25(16)	C3	C4	S2	117.65(16)
C2	N2	S 1	106.32(16)	C3	C4	C5	120.5(2)
C4	C3	C2	119.0(2)	C5	C4	S2	121.80(17)
01	C5	C4	123.0(2)	01	C7	C8	123.9(2)
C6	C5	01	115.00(19)	C12	C7	O1	115.0(2)
C6	C5	C4	122.0(2)	C12	C7	C8	121.1(2)
N2	C2	C3	126.6(2)	C5	C6	C1	118.4(2)
N2	C2	C1	113.4(2)	C10	C9	C8	120.2(2)
C3	C2	C1	120.1(2)	C7	C12	C11	119.4(2)
C7	C8	S2	123.15(17)	C11	C10	C9	120.2(2)
C7	C8	C9	118.7(2)	C10	C11	C12	120.3(2)
C9	C8	S 2	118.06(18)				

Table S12. Bond Angles for SO-BZT in the crystal.

	H10 Ная	H9 C9 C8 C11 C12 C7 C12 H12	H3 C3 C3 C3 C3 C2 N3 H6	2	
Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	N1	1.637(4)	C1	C6	1.414(6)
S1	N2	1.617(4)	C8	C7	1.396(6)
O1	C7	1.382(5)	C8	С9	1.365(6)
O1	C5	1.385(5)	C4	C3	1.353(6)
O2	C8	1.383(5)	C4	C5	1.441(6)
O2	C4	1.376(5)	C7	C12	1.380(6)
N1	C1	1.329(6)	С9	C10	1.384(7)
N2	C2	1.347(6)	C6	C5	1.352(6)
C2	C1	1.449(6)	C11	C12	1.373(7)
C2	C3	1.407(6)	C11	C10	1.383(7)

Table S13. Bond lengths (Å) for OO-BZT in the crystal.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	S 1	N1	101.1(2)	C3	C4	02	118.3(4)
C7	01	C5	117.7(3)	C3	C4	C5	121.2(4)
C4	O2	C8	118.1(3)	O1	C7	C8	121.8(4)
C1	N1	S 1	105.8(3)	C12	C7	01	118.3(4)
C2	N2	S 1	106.3(3)	C12	C7	C8	119.9(4)
N2	C2	C1	112.9(4)	C8	C9	C10	119.8(4)
N2	C2	C3	126.5(4)	C4	C3	C2	118.3(4)
C3	C2	C1	120.7(4)	C5	C6	C1	118.2(4)
N1	C1	C2	114.0(4)	01	C5	C4	120.5(4)
N1	C1	C6	126.6(4)	C6	C5	01	117.3(4)
C6	C1	C2	119.5(4)	C6	C5	C4	122.2(4)
O2	C8	C7	121.3(4)	C12	C11	C10	120.8(5)
C9	C8	O2	118.4(4)	C11	C12	C7	119.4(4)
C9	C8	C7	120.3(4)	C11	C10	C9	119.7(5)
O2	C4	C5	120.5(4)				

 Table S14. Bond Angles for OO-BZT in the crystal.

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