

Enhancing the sensitization efficiency of erbium doped organic complexes by heavy halogen substitution

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Chemical synthesis and characterization of zinc-containing chromophores

Zn(FBTZ)₂ was prepared from pentafluoroaniline and the known^{S1} 6-methoxy-2,3,4,5-tetrafluorobenzyl chloride, as previously described;^{S2} Zn(Cl-FTPIP)₂ and Zn(Br-FTPIP)₂ were prepared analogously.

Zn(Cl-FBTZ)₂

Yellow solid, mp > 300 °C

$\nu_{\max}/\text{cm}^{-1}$ 1659, 1493, 1403, 1269, 1252, 1198, 1053, 1005, 942, 830, 752, 667;

δ_{F} (367 MHz, DMSO-*d*₆) -119.1 (dd, *J* 16, 3 Hz), -142.6 - -142.7 (m, 2F), -152.0 (dd, *J* 21, 16 Hz), -159.7 (td, *J* 23, 3 Hz), -167.6 (dt, *J* 23, 11 Hz), -187.6 (m).

Found: C, 37.53; H, <0.10; N, 3.36. C₂₆Cl₂F₁₄N₂O₂S₂Zn requires C, 37.24; H, 0.00; N, 3.34%.

HRMS (APCI) *m/z* Found: 836.7920; C₂₆HCl₂F₁₄N₂O₂S₂Zn⁺ [M+H⁺] requires 836.7919.

Zn(Br-FBTZ)₂

Yellow solid, mp > 300 °C

$\nu_{\max}/\text{cm}^{-1}$ 1660, 1479, 1399, 1307, 1264, 1245, 1194, 1133, 1096, 1049, 1001, 930, 824, 772, 748, 691, 638, 630, 605.

δ_{F} (367 MHz, DMSO-*d*₆) -111.5 (dd, *J* 16, 3 Hz), -135.4 (dd, *J* 21, 3 Hz), -142.5 (ddd, *J* 24, 11, 3 Hz), -151.9 (dd, *J* 21, 16 Hz), -159.7 (td, *J* 23, 3 Hz), -167.6 (dt, *J* 23, 11 Hz), -187.6 (td, *J* 23, 12 Hz).

Found: C, 33.56; H, <0.10; N, 3.03. C₂₆Br₂F₁₄N₂O₂S₂Zn requires C, 33.67; H, 0.00; N, 3.02%.

HRMS (APCI) *m/z* Found: 924.6912; C₂₆Br₂F₁₄N₂O₂S₂ZnH⁺ [M+H⁺] requires 924.6909.

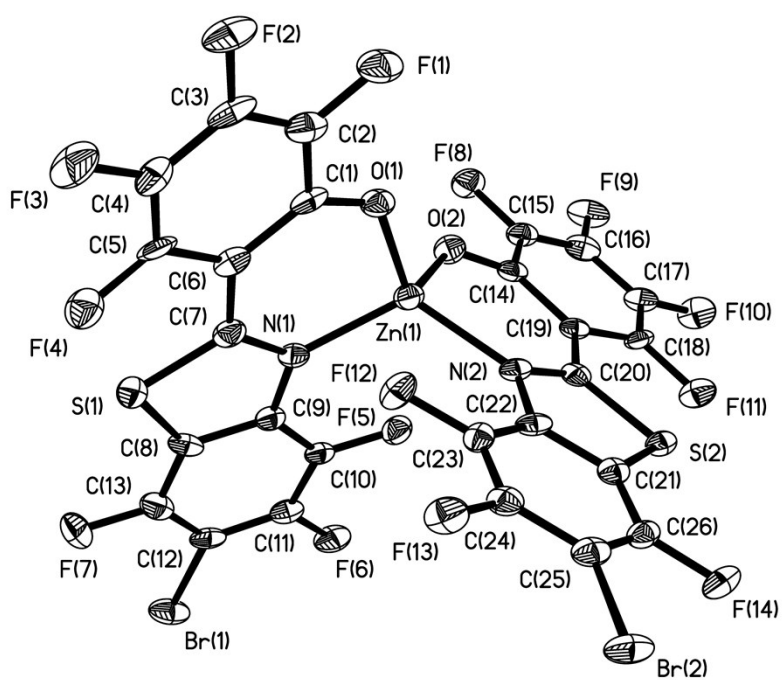


Fig. S1 X-ray crystal structure of Zn(Br-FBTZ)₂. The crystal was prepared by sublimation *in vacuo*.

Table S1. Crystal data and structure refinement for Zn(Br-FBTZ)₂

Empirical formula	C ₂₆ Br ₂ F ₁₄ N ₂ O ₂ S ₂ Zn	
Formula weight	927.59	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	<i>a</i> = 7.7699(18) Å	<i>α</i> = 117.280(18)°.
	<i>b</i> = 13.996(3) Å	<i>β</i> = 94.333(13)°.
	<i>c</i> = 14.391(4) Å	<i>γ</i> = 104.573(5)°.
Volume	1312.6(6) Å ³	
<i>Z</i>	2	
Density (calculated)	2.347 Mg/m ³	
Absorption coefficient	4.274 mm ⁻¹	
<i>F</i> (000)	888	
Crystal size	0.160 x 0.090 x 0.050 mm ³	
Theta range for data collection	1.633 to 27.984°.	
Index ranges	-10 ≤ <i>h</i> ≤ 10, -18 ≤ <i>k</i> ≤ 18, -18 ≤ <i>l</i> ≤ 18	
Reflections collected	20198	
Independent reflections	6136 [<i>R</i> (int) = 0.0765]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	6136 / 0 / 443	
Goodness-of-fit on <i>F</i> ²	1.025	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0622, <i>wR</i> 2 = 0.1460	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1108, <i>wR</i> 2 = 0.1671	
Largest diff. peak and hole	1.836 and -1.084 e Å ⁻³	

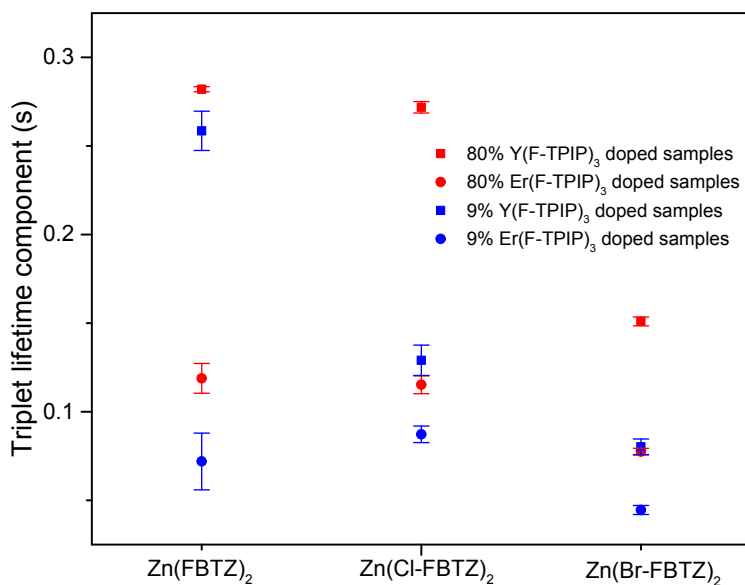


Fig. S2 Triplet lifetime components measured at 80K by a 5 ns pulse laser for Y(F-TPIP)₃, Er(F-TPIP)₃ co-doped with Zn(FBTZ)₂, Zn(Cl-FBTZ)₂ and Zn(Br-FBTZ)₂ respectively. The monitored wavelength is set at 560 nm and the excitation wavelength is 410 nm.

Samples diluted with increasing Y(F-TPIP)₃ concentrations show longer triplet lifetimes, which suggests a reduced effect of triplet-triplet annihilation (TTA) in these samples. Meanwhile, the incorporation of heavier halogen atoms causes a decrease in the triplet lifetime for all Y(F-TPIP)₃ doped films; this indicates that the substitution introduces more efficient spin-coupling due to the heavy atom effect, hence more efficient intersystem crossing (ISC). The Er(F-TPIP)₃ doped samples show consistently shorter triplet lifetimes compared to their Y(F-TPIP)₃ doped counterparts which implies efficient energy transfer from chromophore to erbium ions. Moreover, the fact that the 80% Er(F-TPIP)₃ doped samples still have longer triplet lifetime than 9% Er(F-TPIP)₃ doped samples indicates the TTA process and the coupling from triplets to erbium ions are competitive in these samples. The triplet lifetime measured by the 5 ns pulse laser is consistent with the result measured by a 407 nm CW laser with 50 ms pulse width.

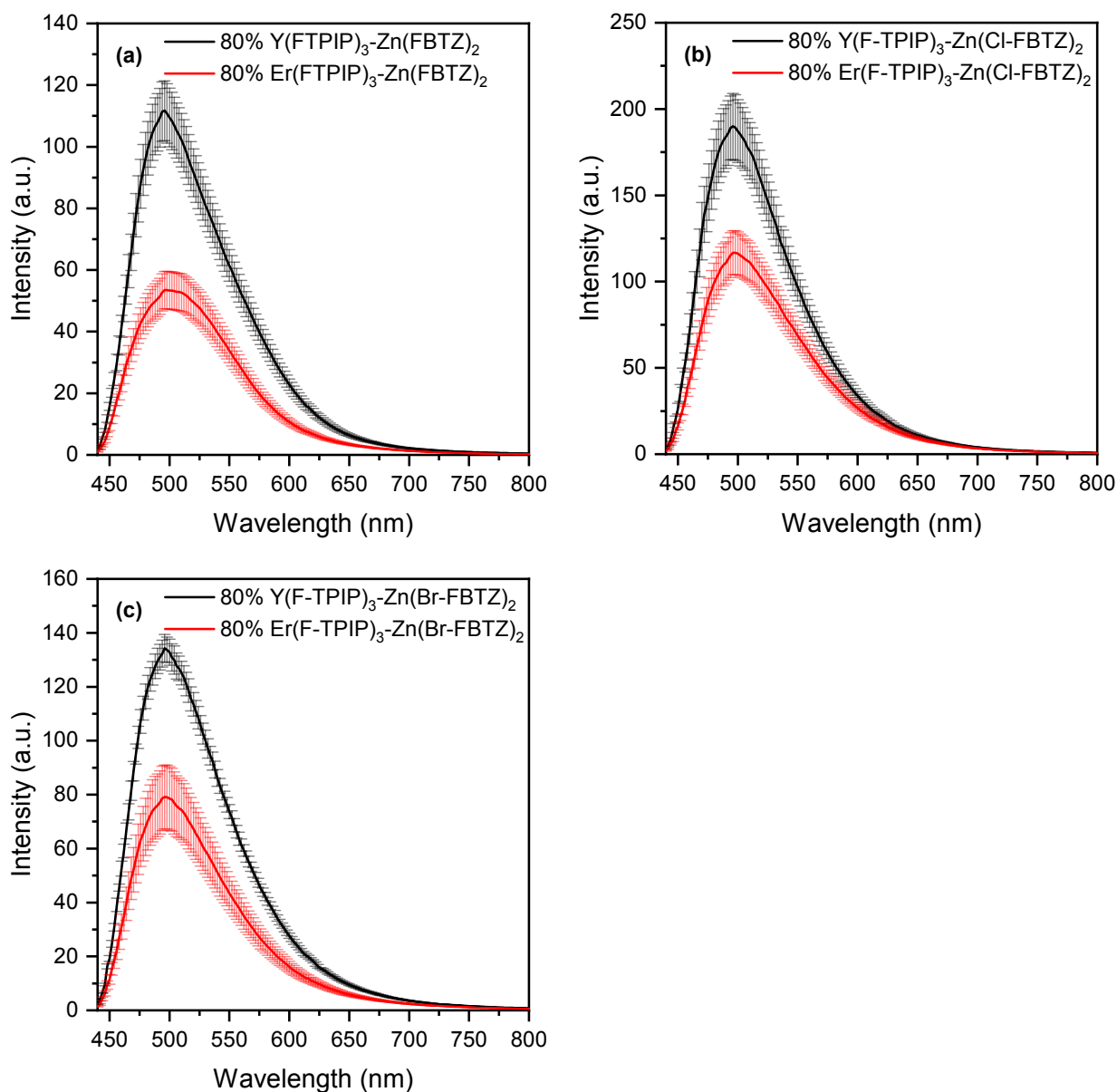


Fig. S3 Photoluminescence spectra comparison between $\text{Y}(\text{F-TPIP})_3$ doped and $\text{Er}(\text{F-TPIP})_3$ doped $\text{Zn}(\text{FBTZ})_2$, $\text{Zn}(\text{Cl-FBTZ})_2$ and $\text{Zn}(\text{Br-FBTZ})_2$ samples at room temperature.

The photoluminescence spectra were recorded at room temperature using a 407 nm CW laser as the excitation light source. The optical path was kept identical during the measurement to have comparable results with the samples mounted behind an aperture in a fixed sample plate. In order to obtain quantitative differences in intensity between a pair of sample each sample was measured three times with alternate measurements on a $\text{Y}(\text{F-TPIP})_3$ doped sample and then the corresponding $\text{Er}(\text{F-TPIP})_3$ doped sample. The data obtained from the three measurements were averaged and the standard error for each set of measurements used as the error bars in Fig. S3. As shown in Fig. S3, the erbium ions can effectively quench singlet emission for all three chromophores, which indicates energy transfer from singlets to erbium ions.

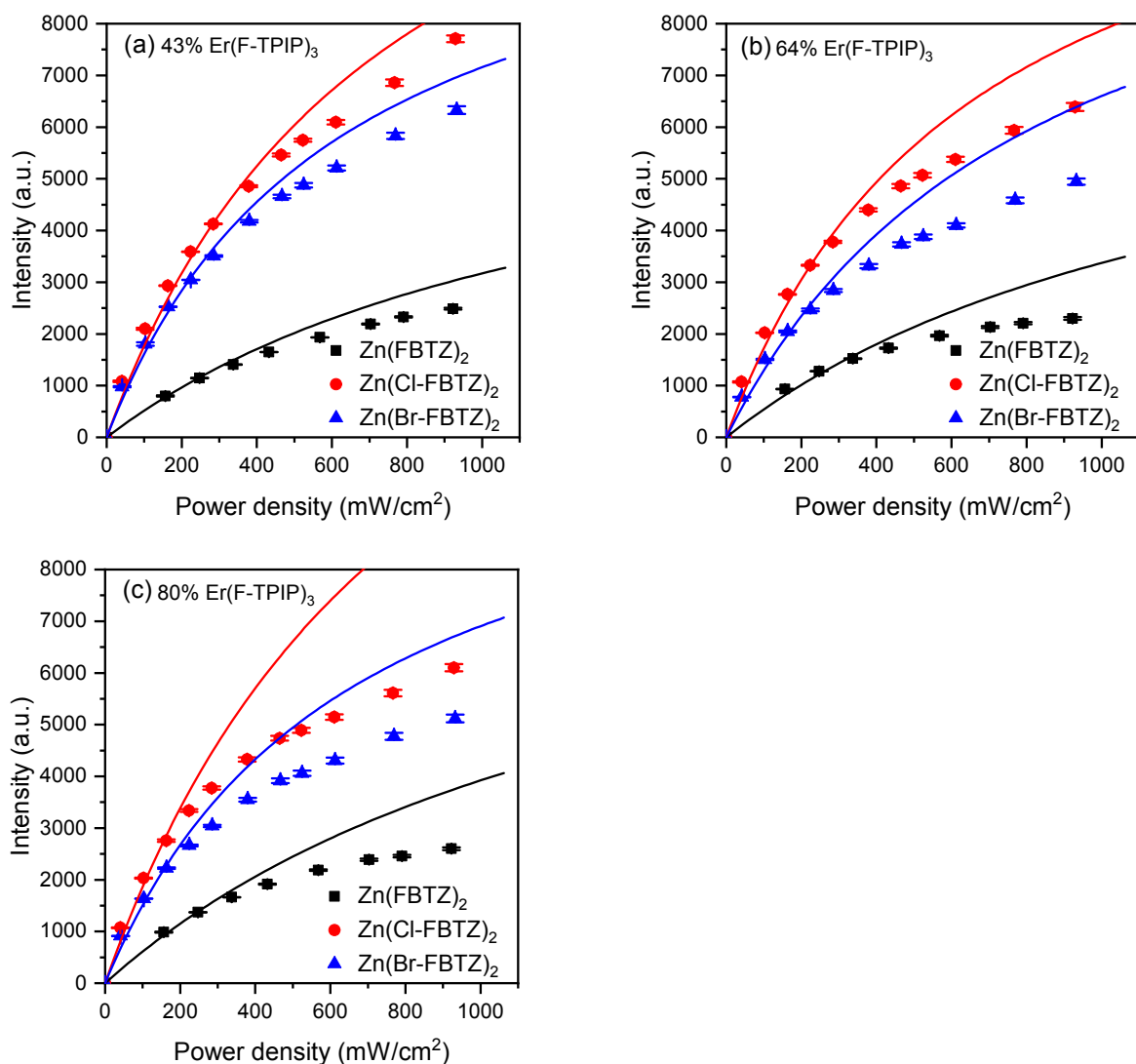


Fig. S4 Sensitisation data for the (a) 43%, (b) 64% and (c) 80% Er(F-TPIP)₃ doped films for each chromophore. The solid lines are the fits from the model.

At higher erbium concentrations the data starts to fall below the model predictions at high 407 nm pump intensities due to the contribution of Er-Er interactions as an additional quenching route. The erbium-erbium interactions become more significant as Er(F-TPIP)₃ concentration and excitation power increase.

References

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