Supplementary Materials

A Practical Hydrazine-Carbothioamide-Based Fluorescent Probe for the Detection of Zn^{2+}: Applications to Paper Strip, Zebrafish and Water Samples

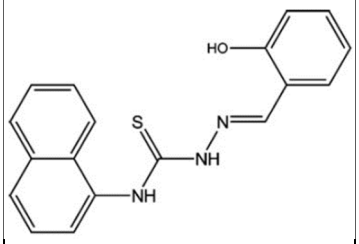
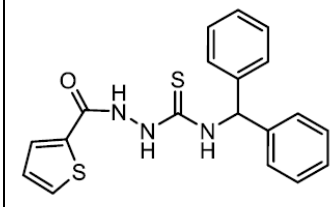
Boeon Suh [1], Dongkyun Gil [1], Sojeong Yoon [2], Ki-Tae Kim [2,*] and Cheal Kim [1,*]

[1] *Department of Fine Chem, Seoul National University of Science and Technology, Seoul 01811, Korea; ssbbee95@naver.com (B.S.); prmodel0131@seoultech.ac.kr (D.G.)*

[2] *Department of Environment Engineering, Seoul National University of Science and Technology, Seoul 01166, Korea; sojung5571@gmail.com*

* *Correspondence: ktkim@snut.ac.kr (K.-T.K.); chealkim@snut.ac.kr (C.K.); Tel.: +82-2-962-6642 (K.-T.K.); Tel.: +82-2-971-6680 (C.K.); Fax: +82-2-972-9149 (K.-T.K.)*

Table S1. Examples of hydrazine-carbothioamide-based fluorescence chemosensors for detecting Zn^{2+}.

No.	Structure	Detection Limit (μM)	Reaction Media	Application			Ref.
				Zebrafish	Water Sample	Test-Strip	
1		0.75	MeCN:H_2O=1:9	No	No	No	[1]
2		1.03	MeOH:HEPES buffer = 9:1	No	No	No	[2]
3		No data	MeCN	No	No	No	[3]
4		0.5	Tris-HCl:ethanol=3:7	No	Yes	No	[4]
5		0.67	PBS buffer	YES	YES	NO	[5]

6		0.39	bis-tris buffer	YES	YES	YES	This work

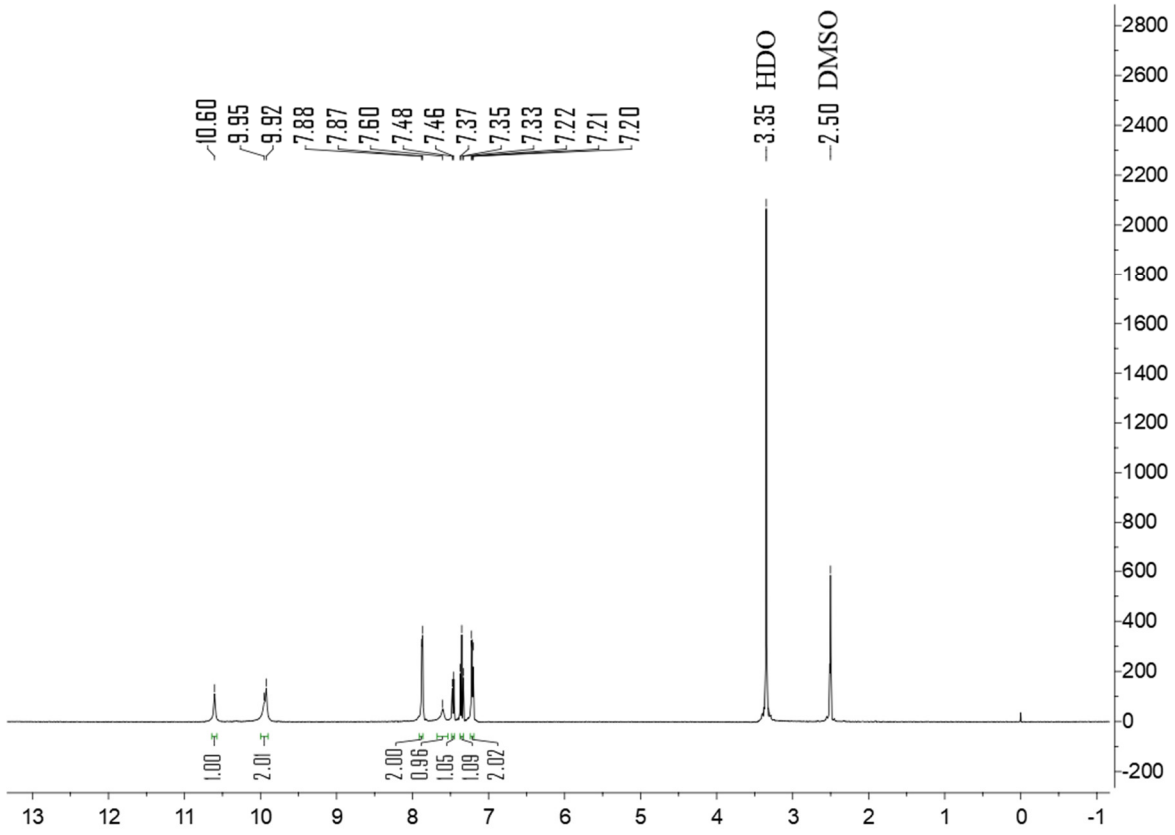


Figure S1. ^{1}H NMR spectrum of **TCC**.

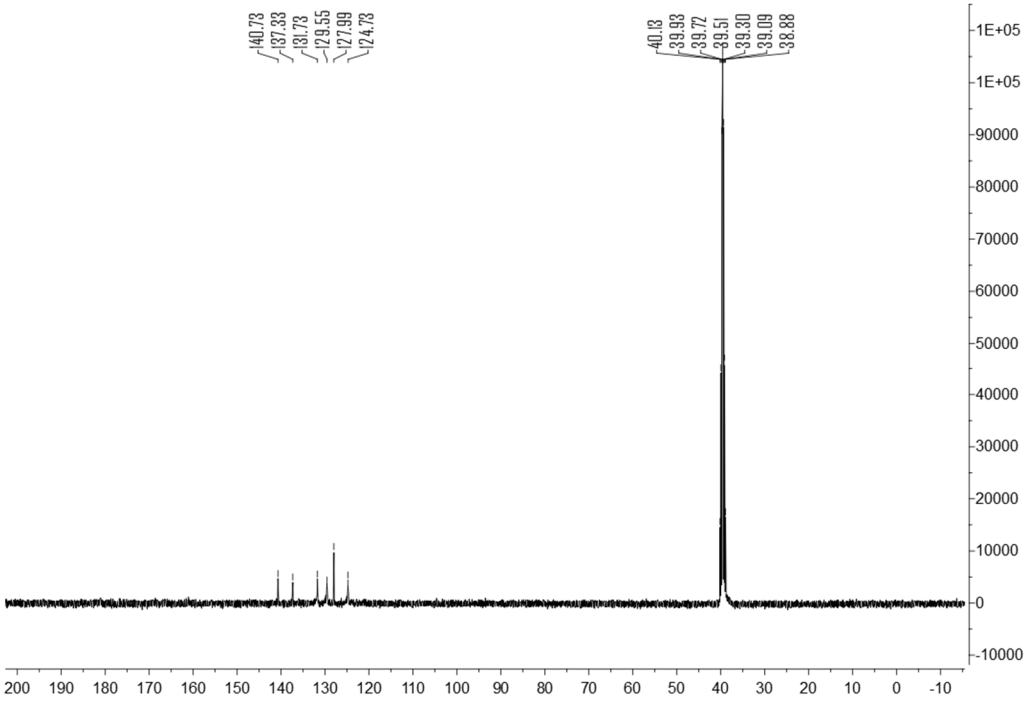


Figure S2. ^{13}C NMR spectrum of **TCC**.

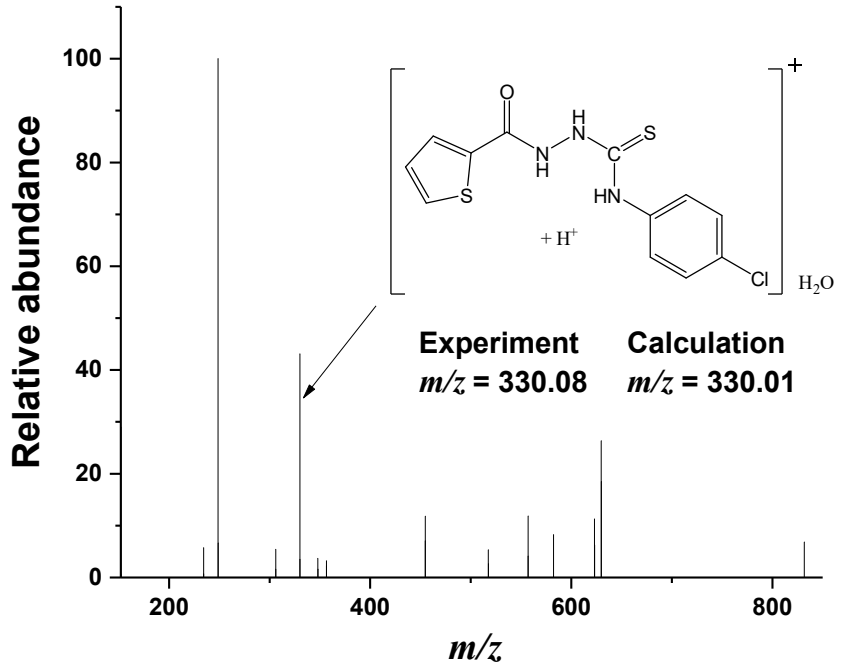


Figure S3. Positive-ion ESI-mass spectrum of **TCC** (100 μM).

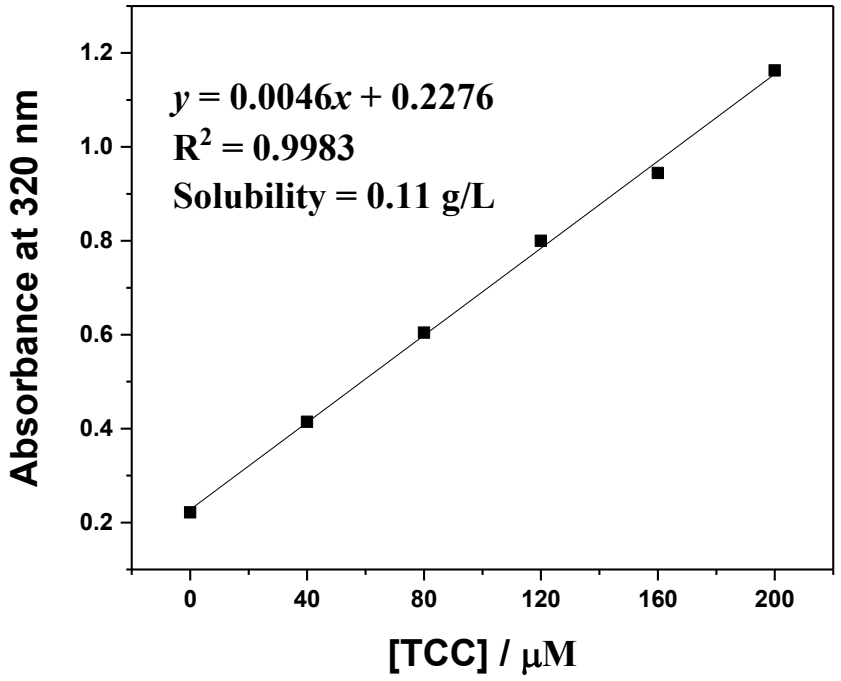


Figure S4. Solubility of **TCC** in distilled water based on the absorbance at 320 nm. Solubility was calculated to the **TCC**-saturated solution with linear fitting curve of **TCC** (0, 40 ,80, 120, 160, 200 μM).

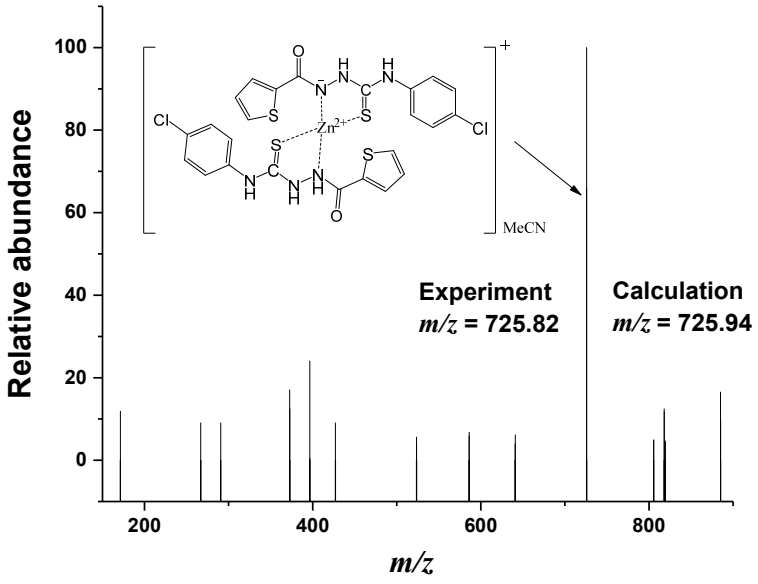


Figure S5. Positive-ion ESI-mass spectrum of **TCC** (100 μM) upon addition of Zn^{2+} (1 equiv).

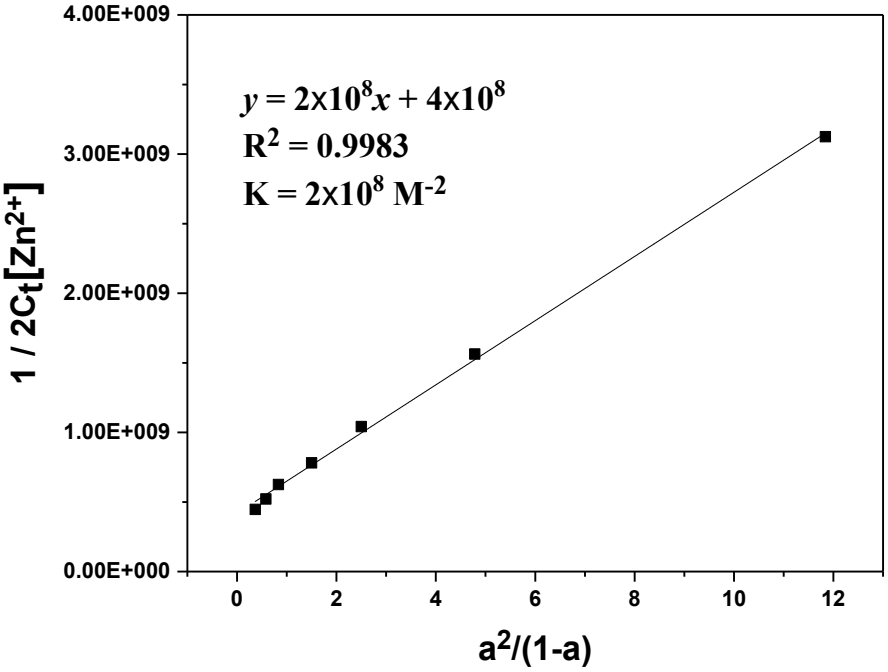


Figure S6. Li's equation plot (at 450 nm) of **TCC** (40 μM) based on fluorescence titration, assuming 2:1 stoichiometry for association between **TCC** and Zn^{2+}.

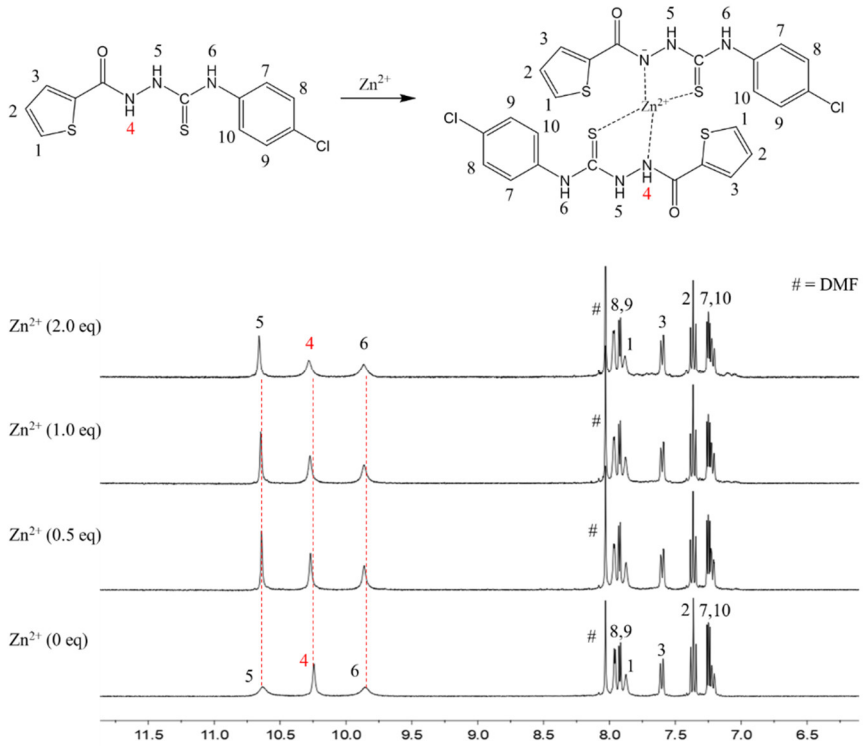


Figure S7. ^{1}H NMR titration of **TCC** (10 mM) upon addition of different amounts of Zn^{2+} (0-2.0 equiv).

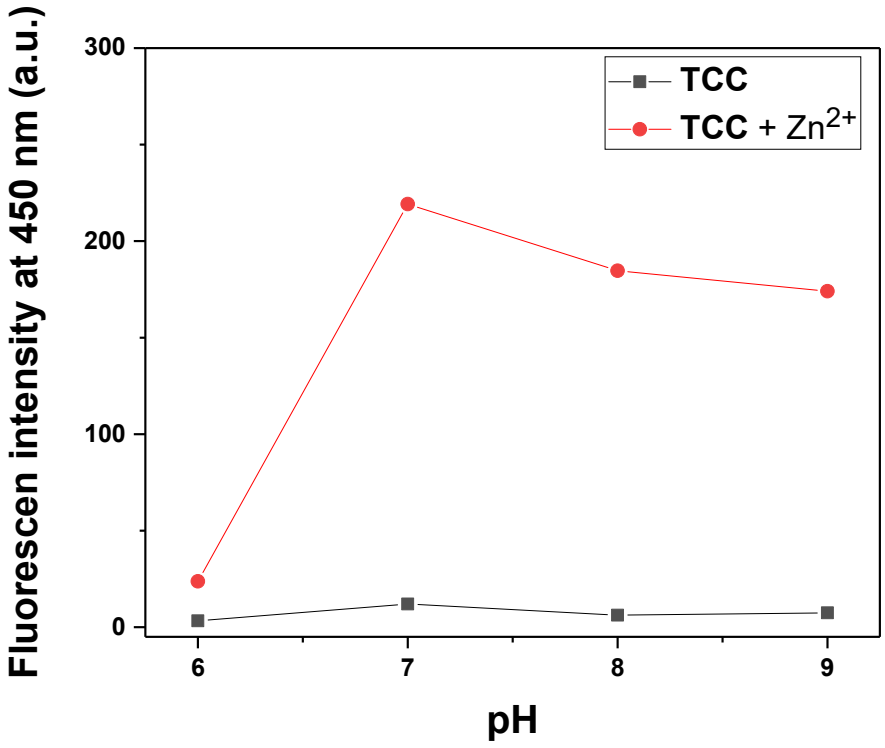


Figure S8. Fluorescence intensity of **TCC** and **TCC**-Zn^{2+} at pH range of 6 to 9 (λ_{ex} = 320 nm).

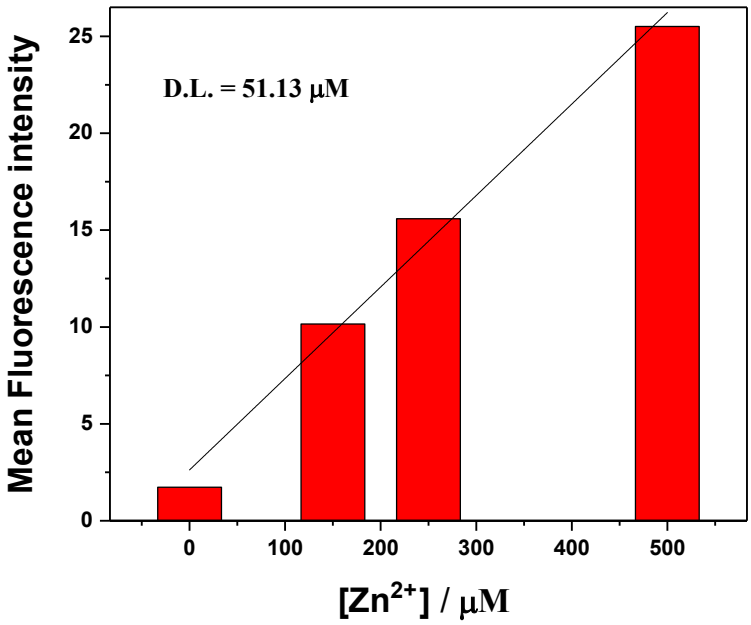
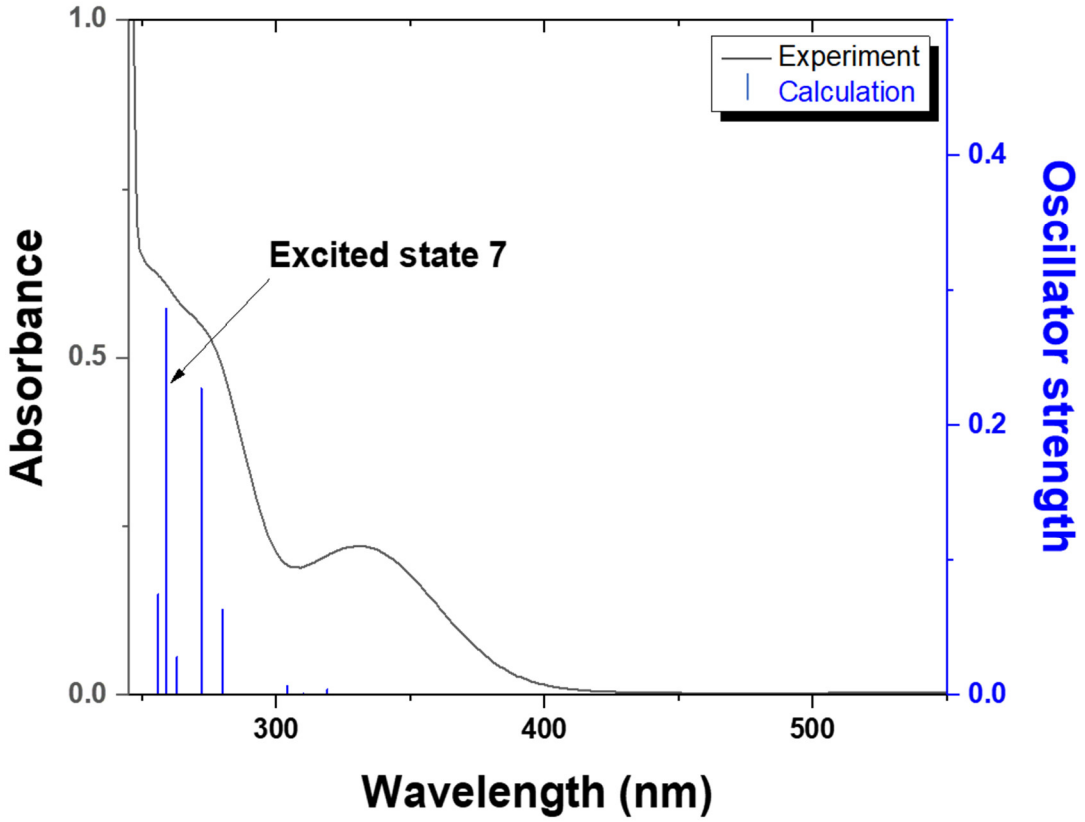


Figure S9. Quantification of mean fluorescence intensity in Figure 8 (a_2, b_2, c_2 and d_2).

(a)



(b)

Excited state 7	Wavelength (nm)	Percent (%)	Main Character	Oscillator strength
H-3 → L	259.1	61%	π → π*	0.2861
H-4 → L		17%	π → π*	
H-6 → L		13%	π → π*	

Figure S10. (**a**) The theoretical excitation energies and the experimental UV-vis spectrum of **TCC**. (**b**) The major electronic transition energies and molecular orbital contributions of **TCC**.

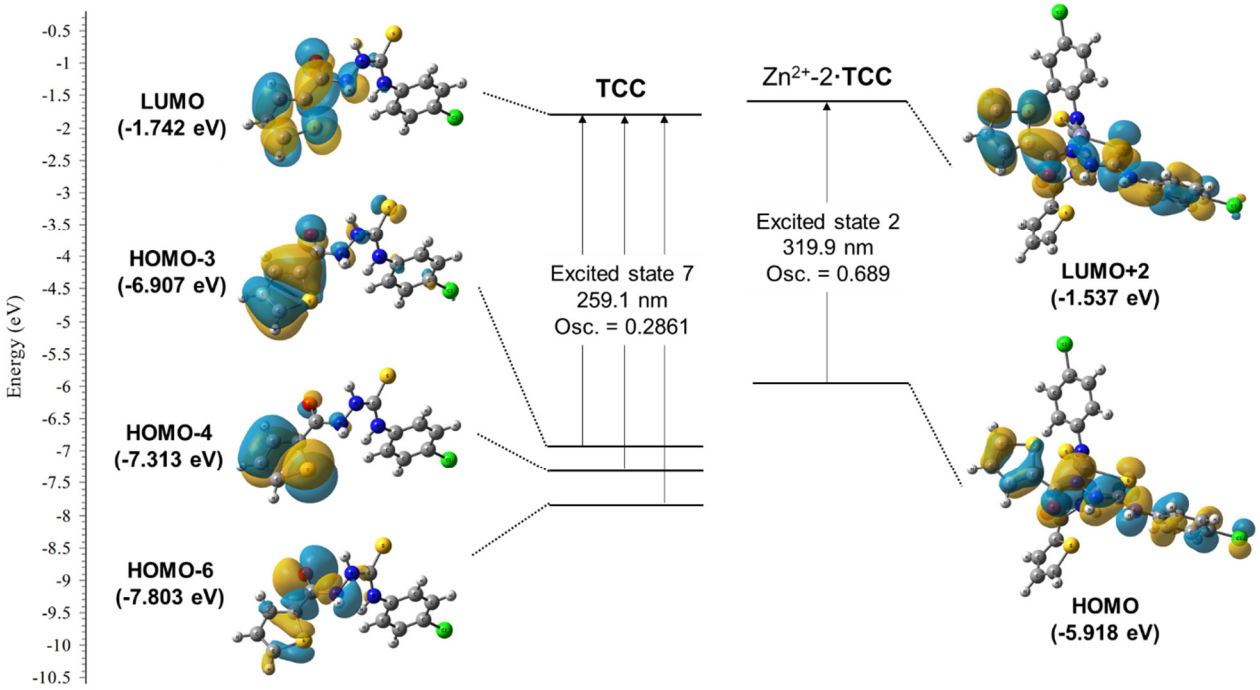
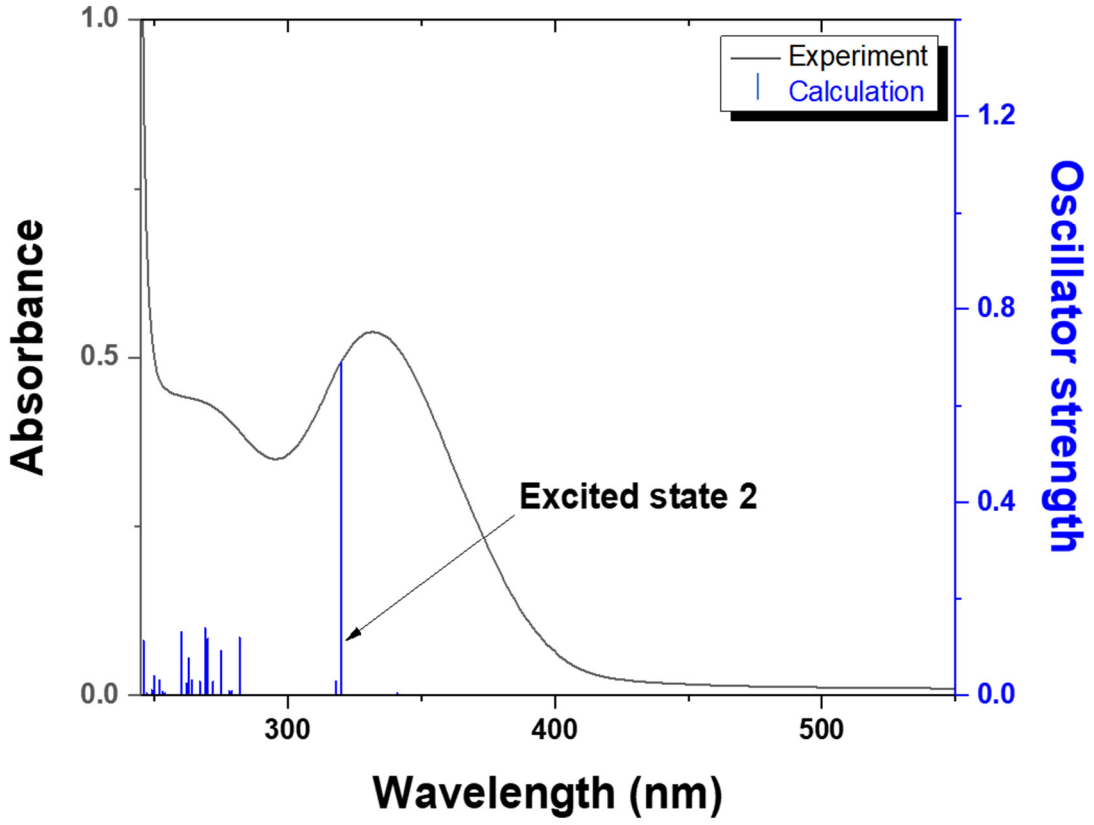


Figure S11. The major molecular orbital transitions and excitation energies of **TCC** and Zn^{2+}-2·**TCC** complex.

(a)



(b)

Excited state 2	Wavelength (nm)	Percent (%)	Main Character	Oscillator strength
H→ L+2	319.9	96%	$\pi \rightarrow \pi^*$	0.689

Figure S12. (**a**) The theoretical excitation energies and the experimental UV-vis spectrum of Zn^{2+}-2·**TCC** complex. (**b**) The major electronic transition energies and molecular orbital contributions of Zn^{2+}-2·**TCC** complex.