Supplementary Data

Synthesis, crystal structure and DFT study of methylphenyl piperazinyl dithiocarbamato zinc(II) precursor for zinc sulfide nanophotocatalysts used for the degradation of trypan blue and rhodamine 6G dyes

Peter A Ajibade[1]*, Fartisincha P Andrew[1], Thandi B. Mbuyazi[1], Tshephiso R. Papo[1], Krishnan Rajeshwar[2],

[1]*School of Chemistry and Physics, University of KwaZulu-Natal, Private Bag X01, Scottsville, Pietermaritzburg, 3209 South Africa*

[2]*Department of Chemistry & Biochemistry, The University of Texas at Arlington, Arlington, Texas 76109, United States of America*

*Correspondence: ajibadep@ukzn.ac.za

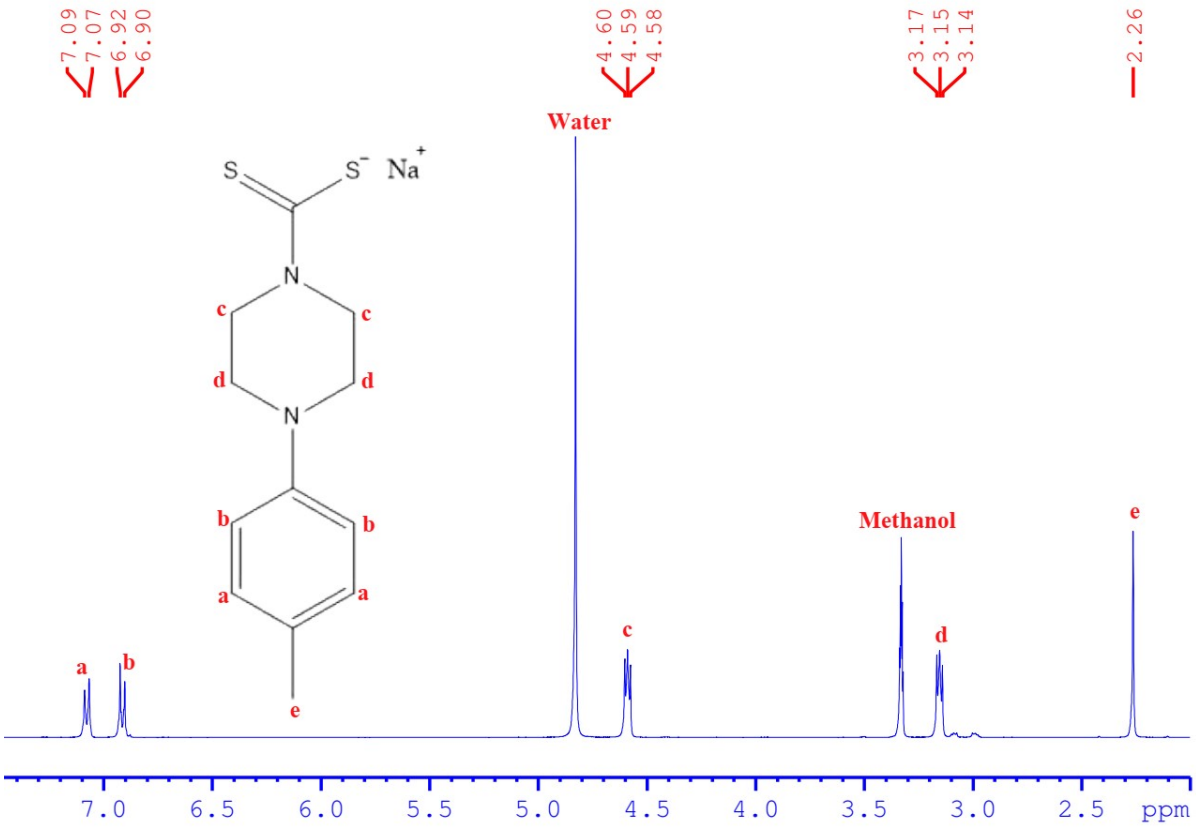

Figure S 1: [1]H NMR spectra of the 1-(4-methylphenyl)piperazinyl dithiocarbamate.

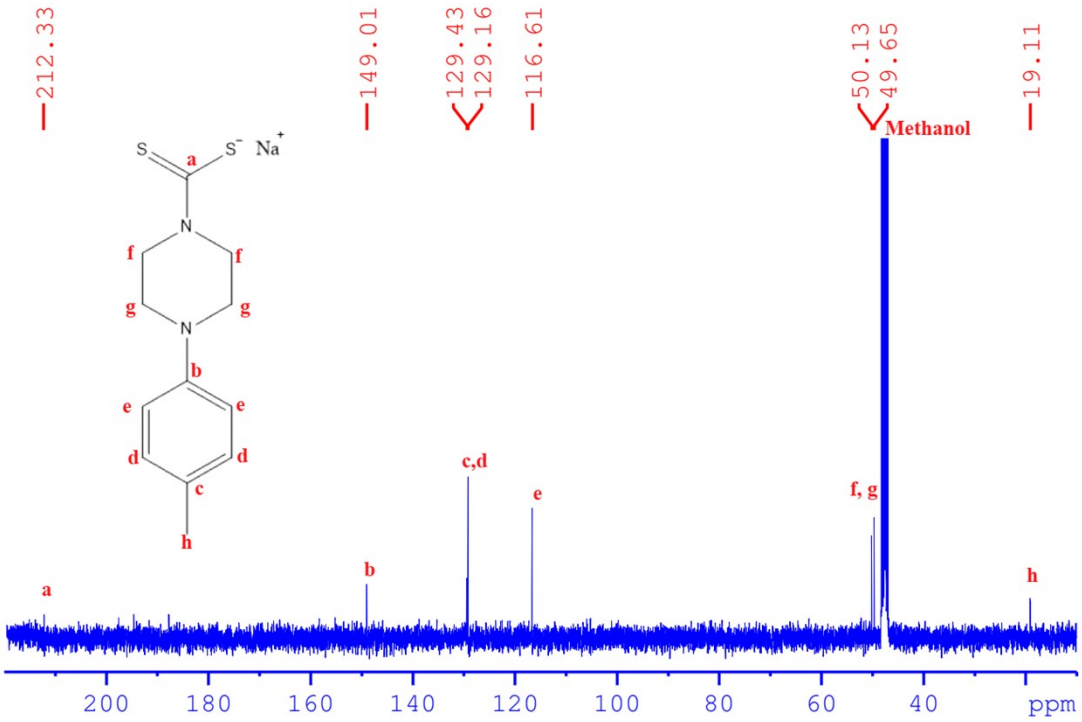

Figure S 2: ^{13}C NMR spectra of the 1-(4-methylphenyl)piperazinyl dithiocarbamate

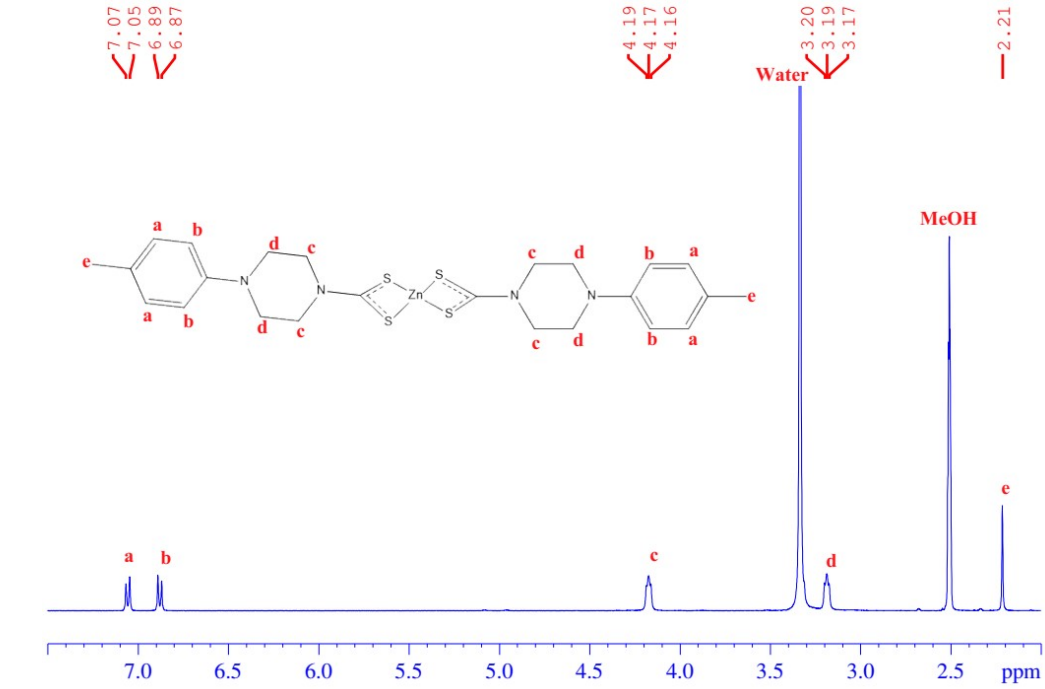

Figure S 3:1H 1-(4-methylphenyl)piperazinyl dithiocarbamate-S,S' Zn(II) complex.

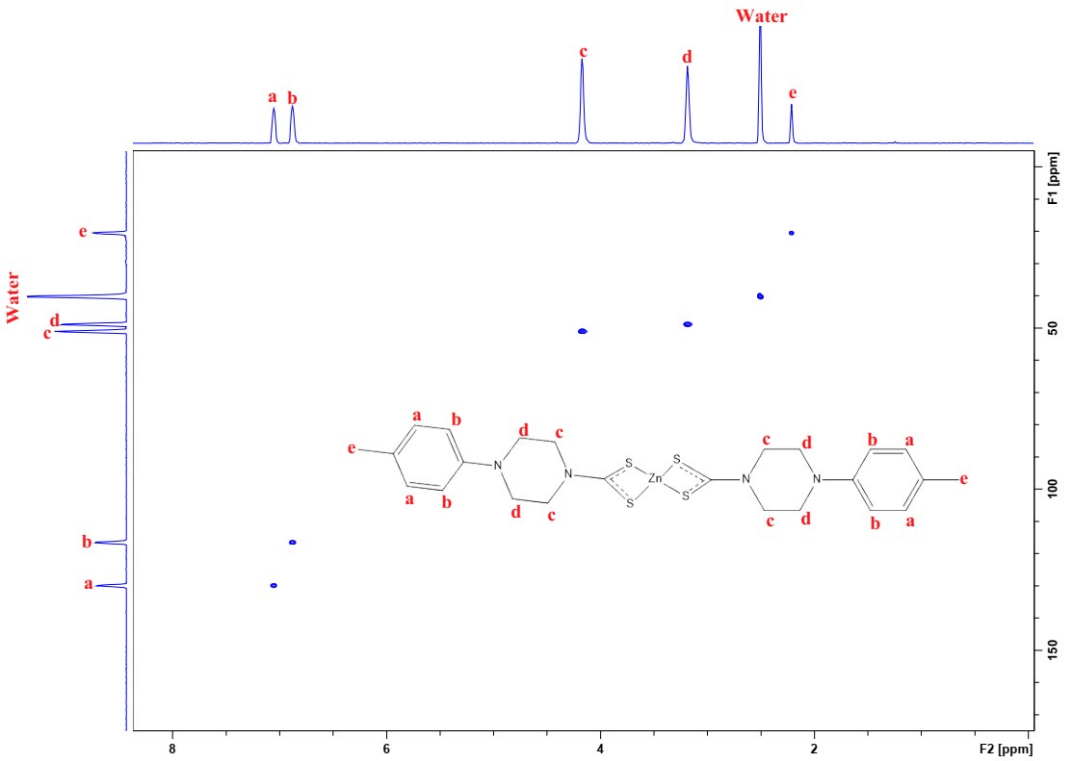

Figure S 4: Heteronuclear single quantum correlation (HSQC) NMR spectra 1-(4-methylphenyl)piperazinyl dithiocarbamate-S,S' Zn(II) complex.

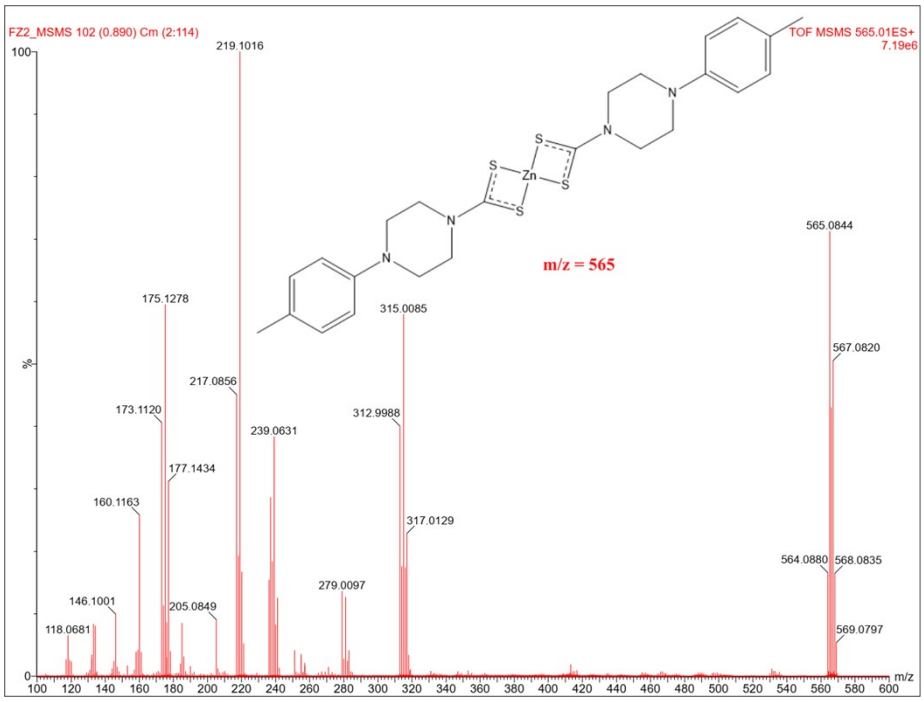

Figure S 5: Mass spectrum of 1-(4-methylphenyl)piperazinyl dithiocarbamate-S,S' Zn(II) complex

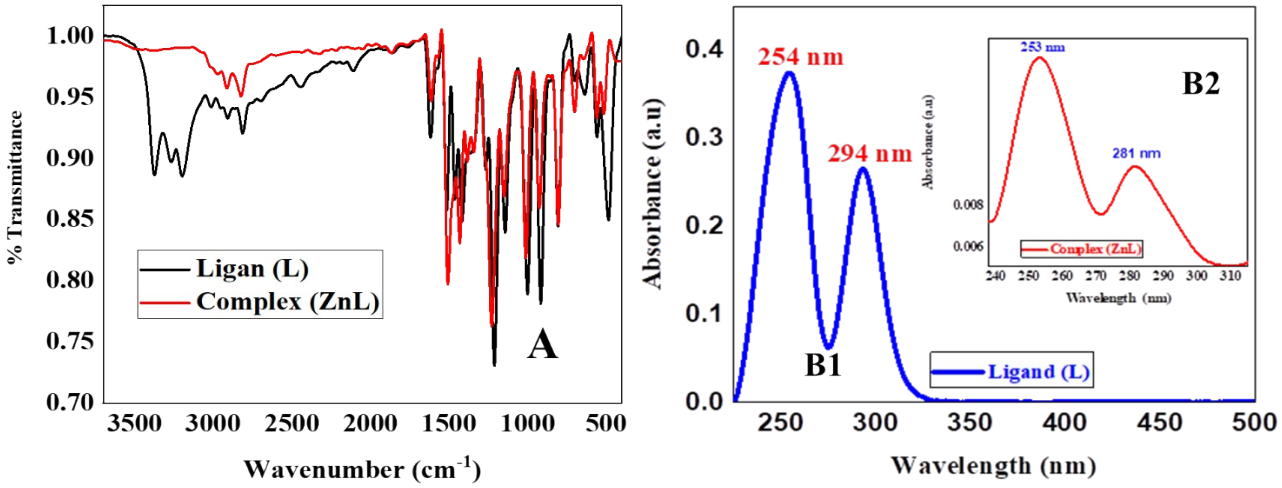

Figure S 6: FTIR spectra of the ligand and the complex (A), UV-Vis spectra of the ligand and the complex (B1 and B2)

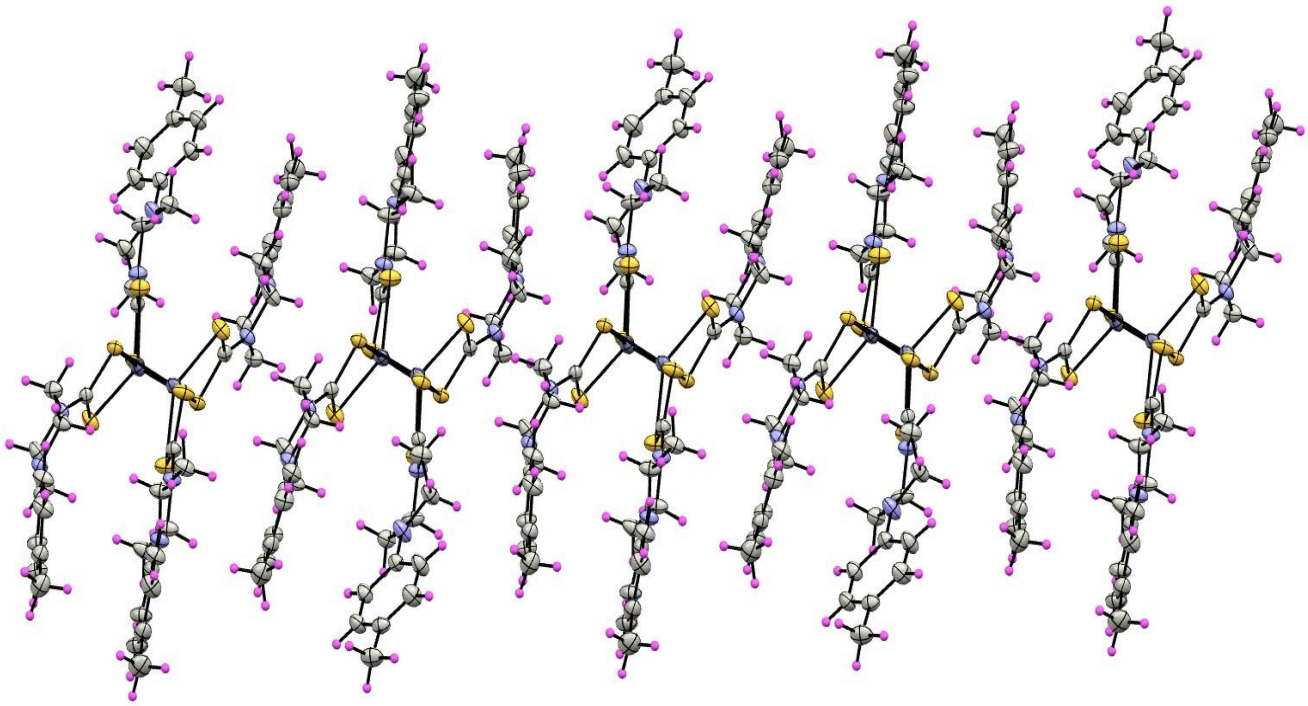

Figure S 7: Short contact stacking viewed down crystallographic a axis

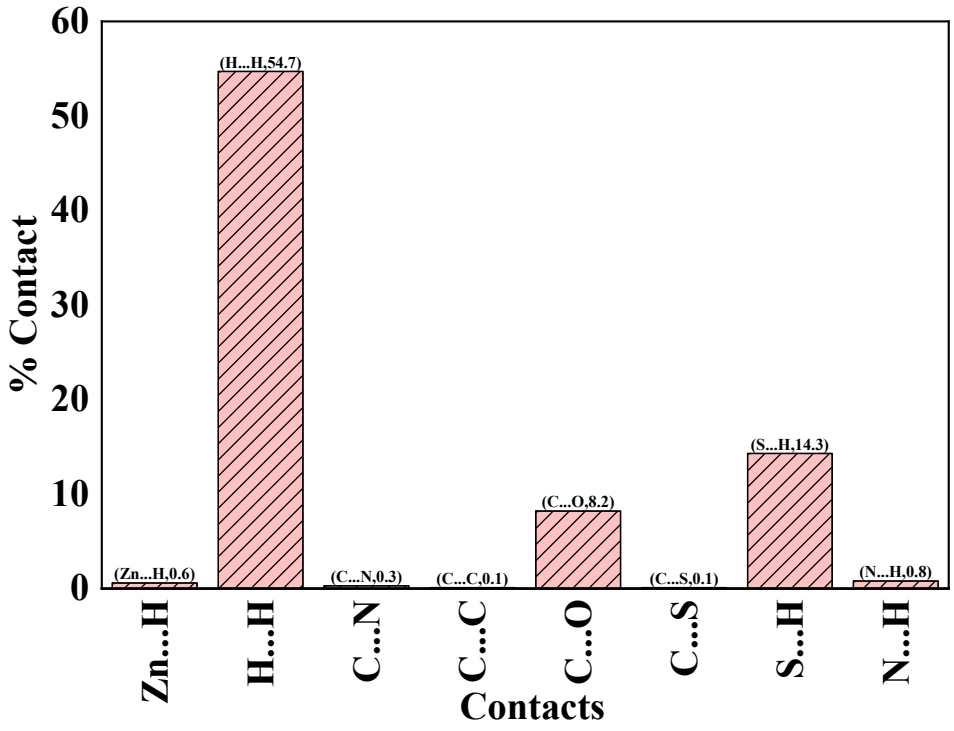

Figure S8: Contacts in 1-(4-methylphenyl)piperazinyl-dithiocarbamator Zn(II) complex

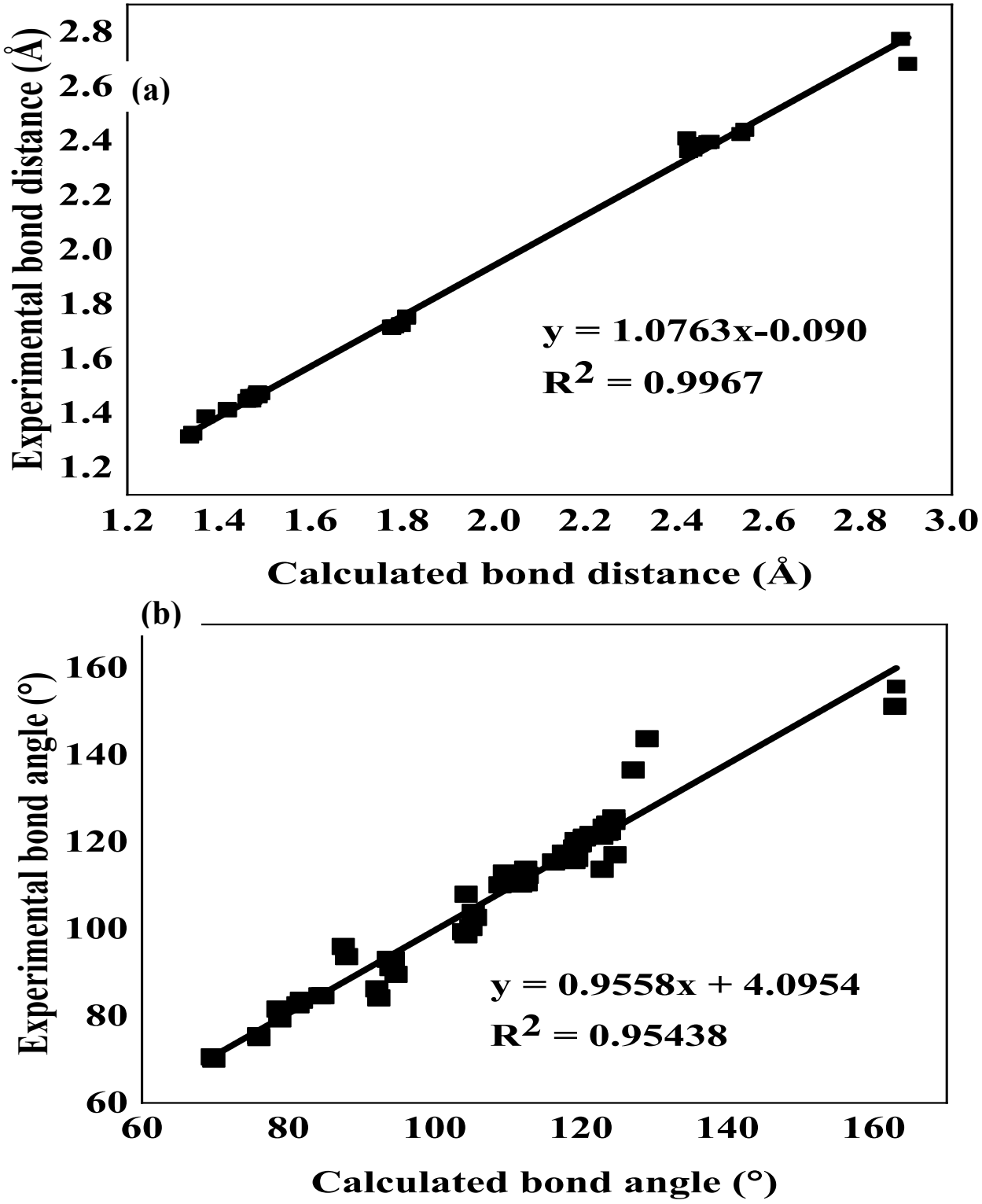

Figure S 9: Correlation graphs between the optimized and experimental bond lengths **(a)** and bond angles **(b)**

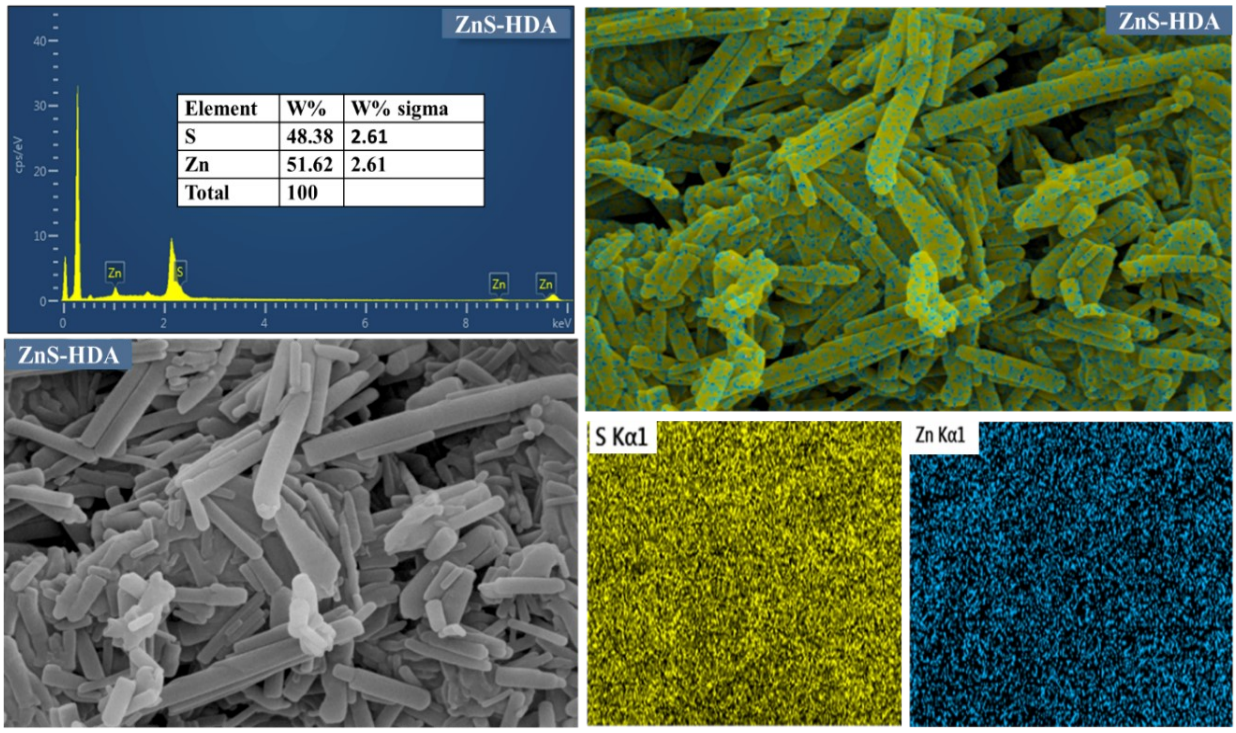

Figure S 10: SEM micrograph and multi-element EDS mapping of ZnS-HDA

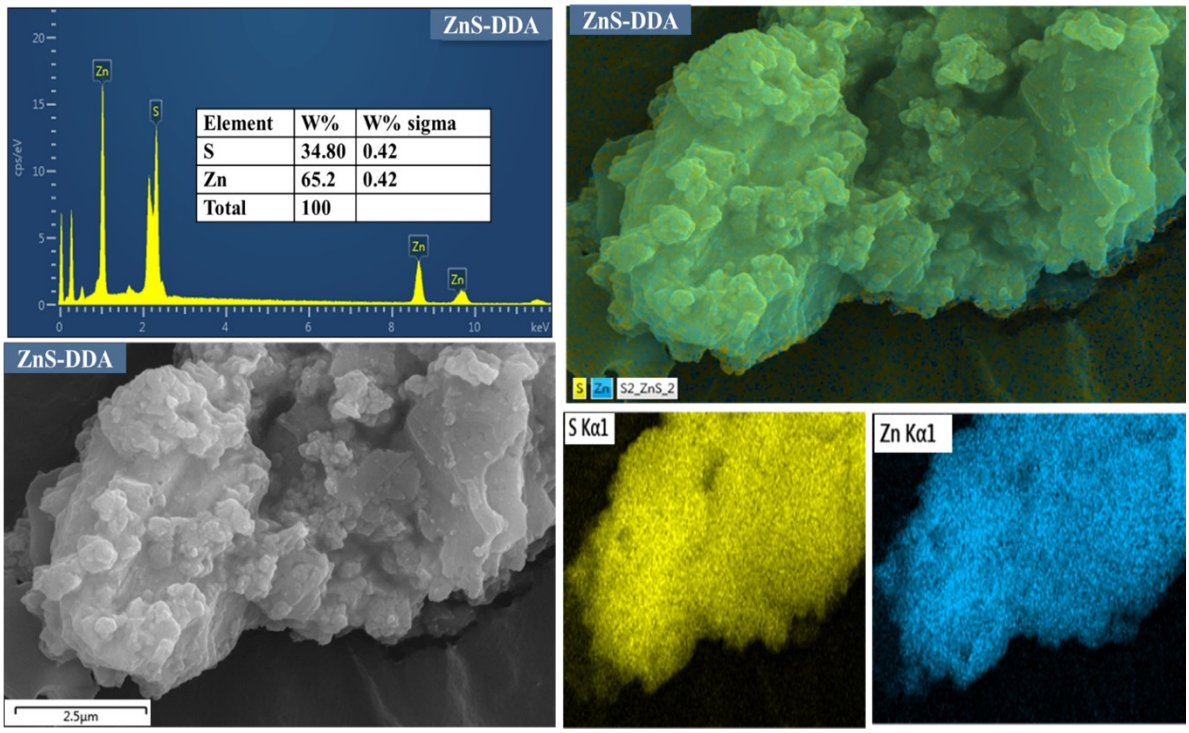

Figure S 11: SEM micrograph and multi-element EDS mapping of ZnS-DDA

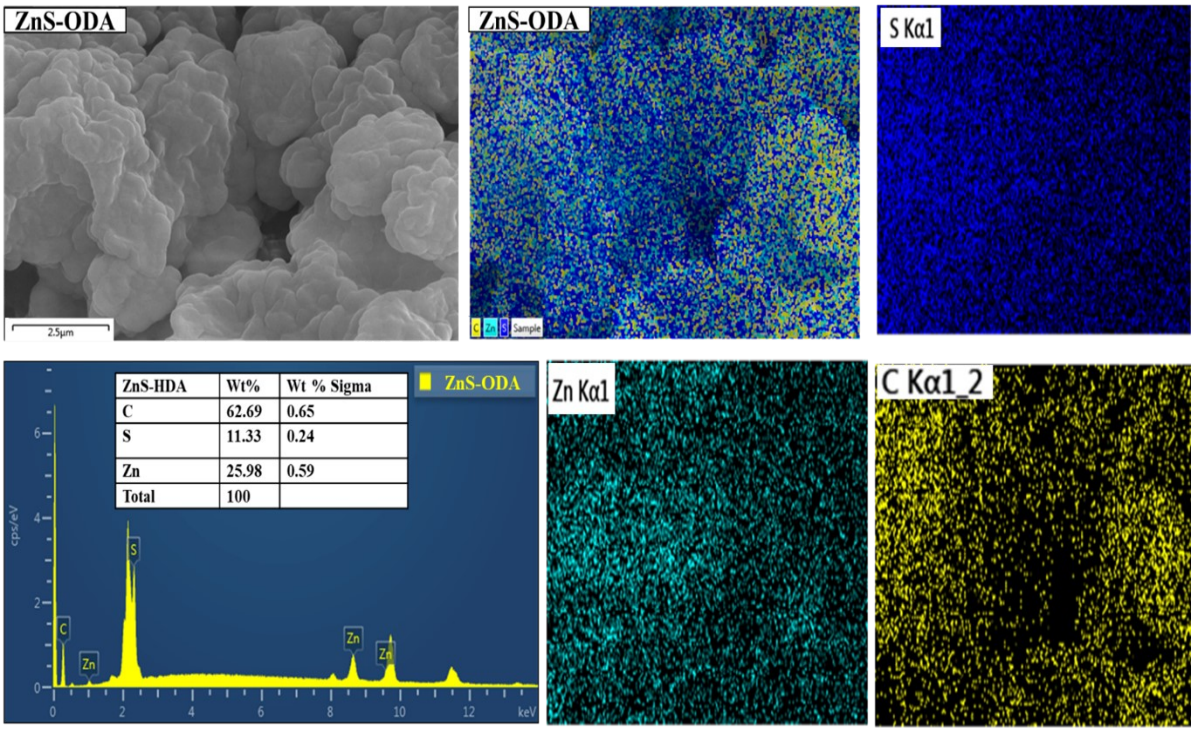

Figure S 12: SEM micrograph and multi-element EDS mapping of ZnS-ODA

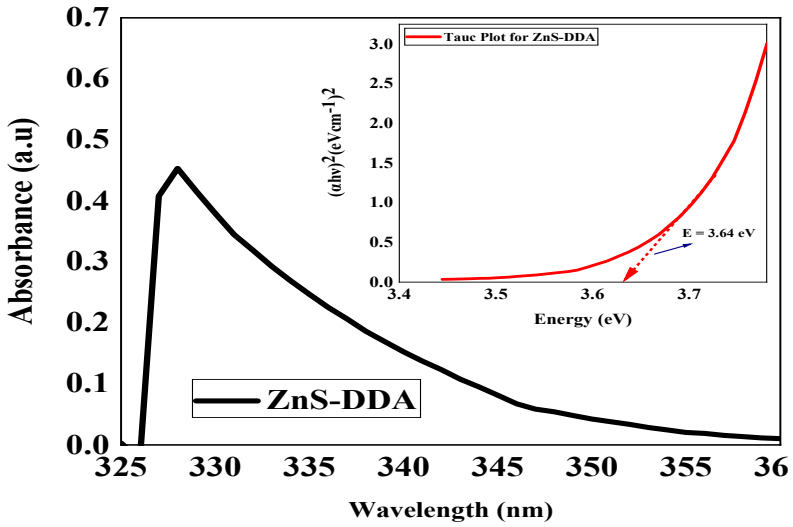

Figure S 13: UV-Visible spectrum and Tauc plot band gap for ZnS-DDA

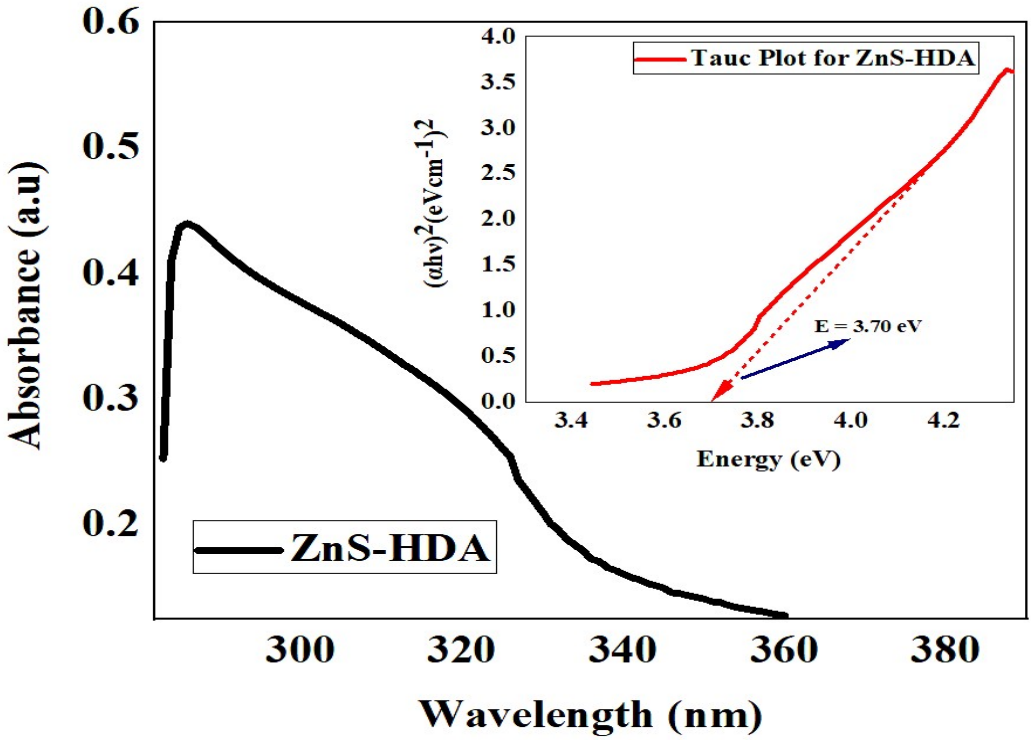

Figure S 14: UV-visible spetcrum and Tauc plot band gap for ZnS-HDA

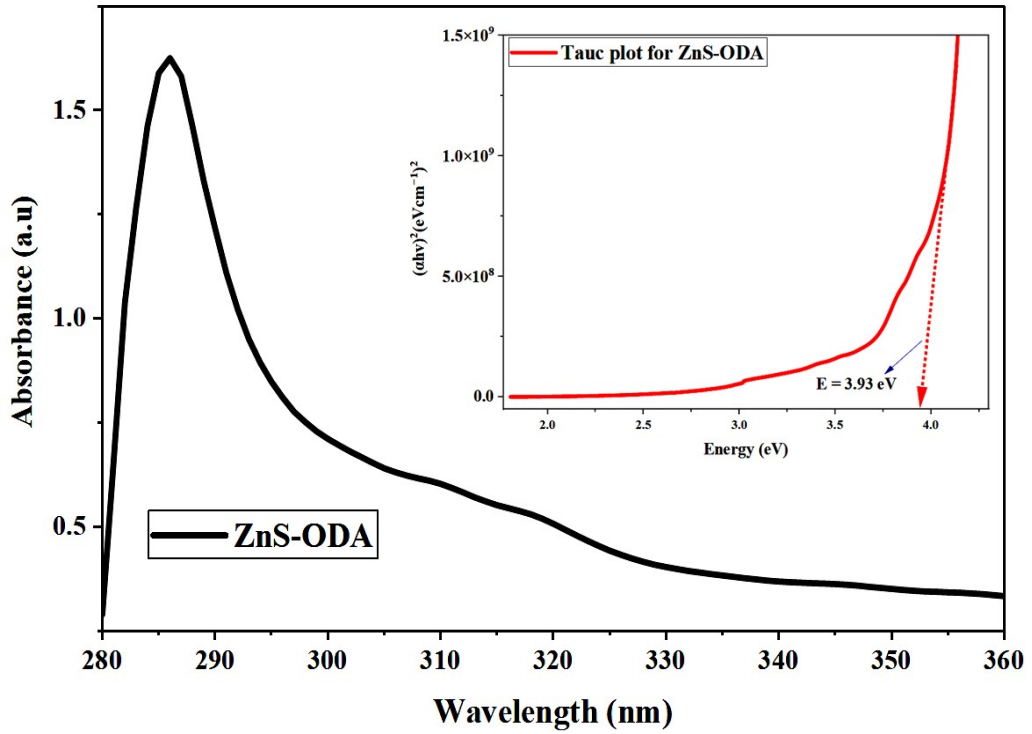

Figure S 15: UV-visible spectrum and Tauc plot band gap for ZnS-ODA

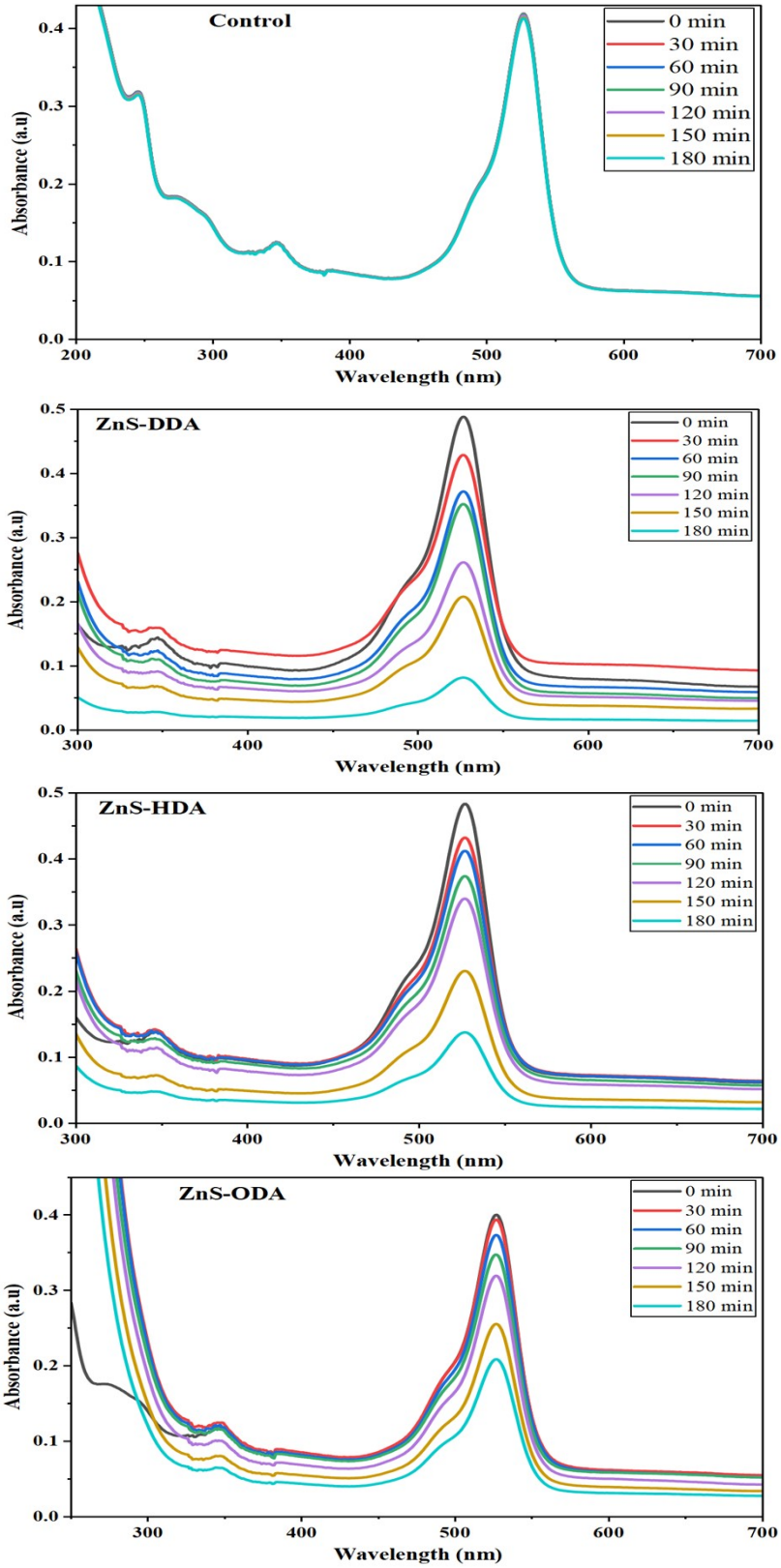

Figure S 16: Absorption spectra of rhodamine 6G degradation by ZnS nanoparticles

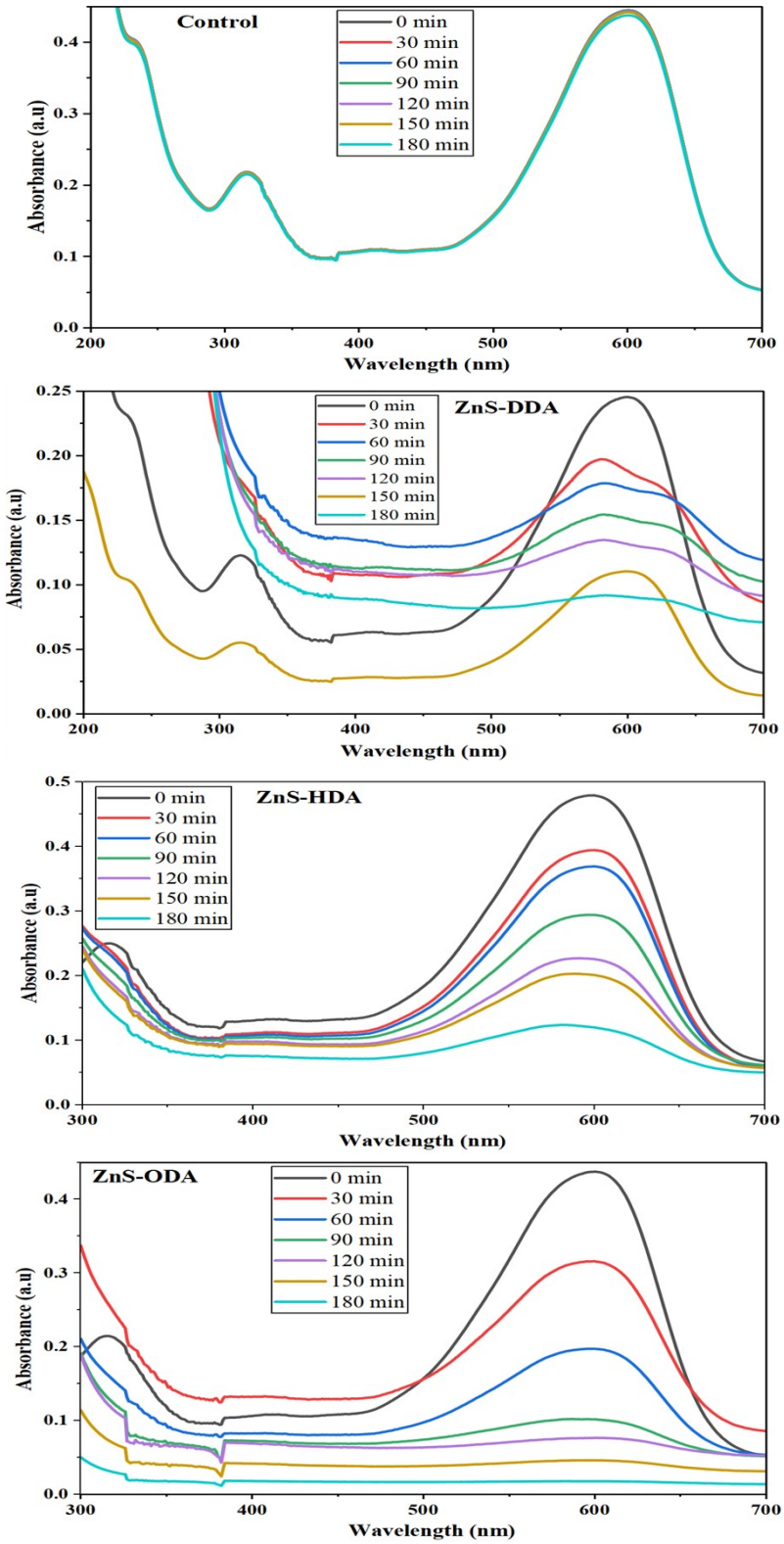

Figure S 17: Absorption spectra of trypan blue degradation by ZnS

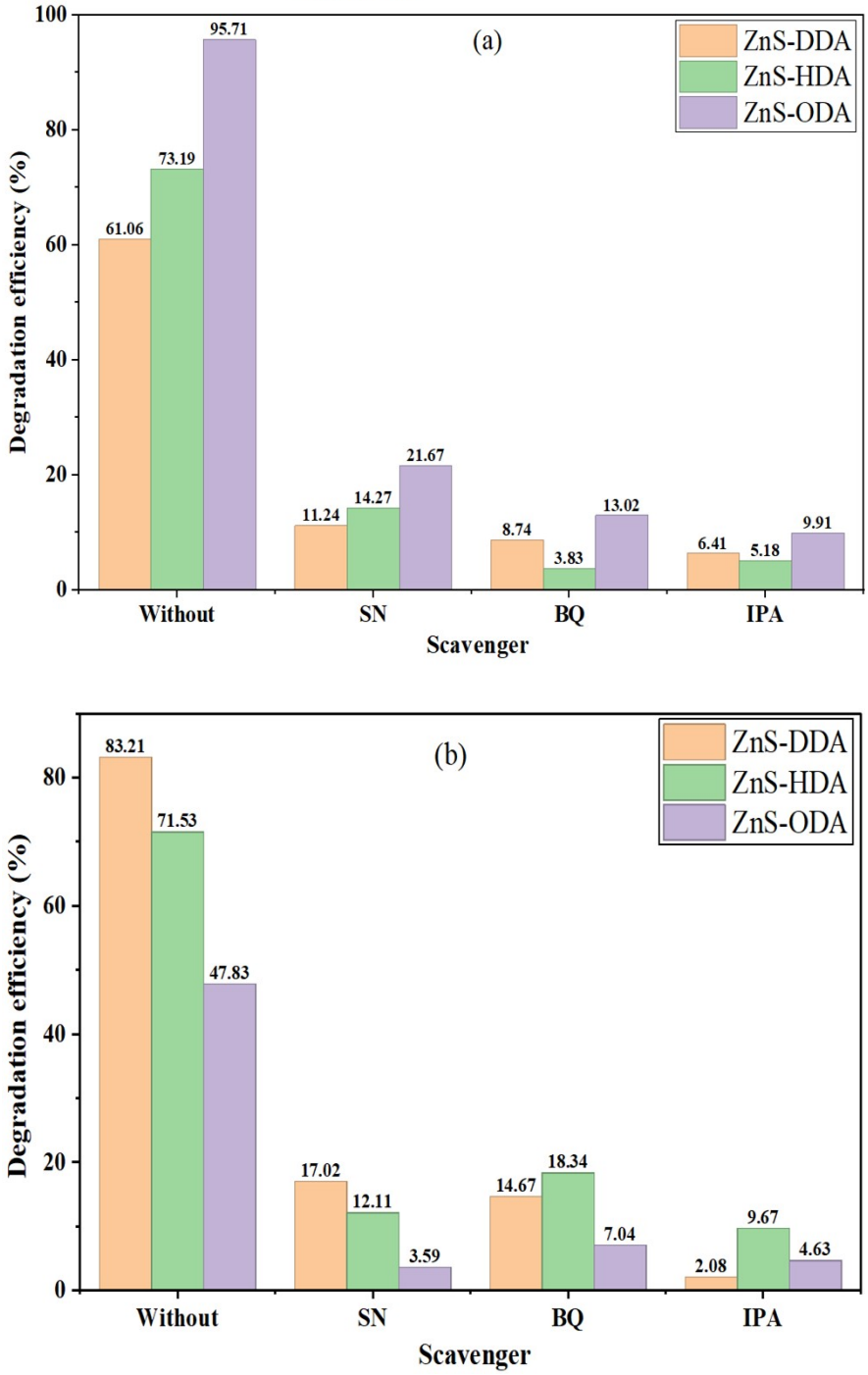

Figure S 18: Effect of scavengers on the photocatalytic degradation of trypan blue (a) and rhodamine 6G (b) using ZnS-DDA, ZnS-HDA, and ZnS-ODA nanoparticles.

Table S1: Comparison of some selected SC-X-ray experimental and DFT calculated bond lengths

Atom	Bond length SC-X-ray (Å)	Bond length DFT (Å)	Absolute error (AE) (Å)	Sqaure absolute error (SAE) (Å)
Z1—S11	2.4399(8)	2.5481	0.1082	0.011707
Z1—S12	2.3672(8)	2.4348	0.0676	0.00457
Z1—S21	2.3617(7)	2.4256	0.0639	0.004083
Z1—S22	2.7738(7)	2.8879	0.1141	0.013019
Z1—S42	2.3939(8)	2.4672	0.0733	0.005373
Z2—S22	2.3958(8)	2.4726	0.0768	0.005898
Z2—S31	2.3880(8)	2.4303	0.0423	0.001789
Z2—S32	2.4242(9)	2.5394	0.1152	0.013271
Z2—S41	2.4082(7)	2.4214	0.0132	0.000174
Z2—S42	2.6818(7)	2.9036	0.2218	0.049195
S11—C11	1.717(2)	1.7789	0.0619	0.003832
S12—C11	1.726(3)	1.7964	0.0704	0.004956
S21—C21	1.717(2)	1.7766	0.0596	0.003552
S22—C21	1.750(2)	1.8099	0.0599	0.003588
S31—C31	1.723(3)	1.7984	0.0754	0.005685
S32—C31	1.718(2)	1.7841	0.0661	0.004369
S41—C41	1.712(2)	1.7774	0.0654	0.004277
S42—C41	1.754(2)	1.8099	0.0559	0.003125
N12—C11	1.324(4)	1.3431	0.0191	0.000365
N12—C111	1.473(3)	1.4916	0.0186	0.000346
N12—C114	1.470(4)	1.484	0.014	0.000196
N13—C112	1.445(3)	1.4613	0.0163	0.000266
N13—C113	1.448(4)	1.4688	0.0208	0.000433
N13—C121	1.388(4)	1.3713	0.0167	0.000279
N21—C21	1.314(3)	1.3361	0.0221	0.000488
N21—C211	1.461(3)	1.4858	0.0248	0.000615
N21—C214	1.476(3)	1.4846	0.0086	7.4E-05
N22—C212	1.462(3)	1.4763	0.0143	0.000204

N22—C213	1.462(3)	1.4669	0.0049	2.4E-05
N22—C221	1.415(4)	1.418	0.003	9E-06
N31—C31	1.327(4)	1.3427	0.0157	0.000246
N31—C311	1.466(4)	1.4835	0.0175	0.000306
N31—C314	1.468(4)	1.483	0.015	0.000225
N32—C312	1.446(4)	1.4719	0.0259	0.000671
N32—C313	1.446(4)	1.4662	0.0202	0.000408
N32—C321	1.411(4)	1.4183	0.0073	5.33E-05
N41—C41	1.314(3)	1.3358	0.0218	0.000475
N41—C411	1.464(3)	1.4856	0.0216	0.000467
N41—C414	1.472(3)	1.4858	0.0138	0.00019
N42—C412	1.455(3)	1.4686	0.0136	0.000185
N42—C413	1.456(3)	1.474	0.018	0.000324
N42—C421	1.410(4)	1.4191	0.0091	8.28E-05
Mean			0.042707	0.003557

Table S 2: Comparison of some selected experimental and DFT calculated bond angles of the zinc(II) complex

Atom	Bond angle SC-X-ray (°)	Bond angle DFT (°)	Absolute error (AE) (°)	Sqaure absolute error (SAE) (°)
S11—Zn1—S12	75.45(3)	75.94	0.49	0.2401
S11—Zn1—S21	107.99(3)	104.31	3.68	13.5424
S11—Zn1—S22	155.70(3)	163.08	7.38	54.4644
S11—Zn1—S42	110.12(3)	108.95	1.17	1.3689
S12—Zn1—S21	136.54(3)	127.14	9.4	88.36
S12—Zn1—S22	89.56(2)	94.74	5.18	26.8324
S12—Zn1—S42	117.04(3)	124.65	7.61	57.9121
S21—Zn1—S21	70.05(2)	69.82	0.23	0.0529
S21—Zn1—S42	102.63(3)	105.6	2.97	8.8209
S22—Zn1—S42	93.64(2)	87.98	5.66	32.0356
S22—Zn2—S31	113.71(3)	122.91	9.2	84.64
S22—Zn2—S32	112.83(3)	109.55	3.28	10.7584

S22—Zn2—S41	100.32(3)	104.95	4.63	21.4369
S22—Zn2—S42	95.97(2)	87.52	8.45	71.4025
S31—Zn2—S32	75.00(3)	75.99	0.99	0.9801
S31—Zn2—S41	143.71(3)	129.06	14.65	214.6225
S31—Zn2—S42	92.89(2)	94.37	1.48	2.1904
S32—Zn2—S41	103.80(3)	105.3	1.5	2.25
S32—Zn2—S42	151.17(3)	162.91	11.74	137.8276
S41—Zn2—S42	70.60(2)	69.63	0.97	0.9409
Zn1—S11—C11	82.55(8)	81.34	1.21	1.4641
Zn1—S12—C11	84.62(8)	84.34	0.28	0.0784
Zn1—S21—C21	93.00(8)	93.68	0.68	0.4624
Zn1—S22—Zn2	84.13(2)	92.38	8.25	68.0625
Zn1—S22—C21	79.29(8)	78.85	0.44	0.1936
Zn2—S22—C21	99.34(8)	103.98	4.64	21.5296
Zn2—S31—C31	84.62(8)	84.74	0.12	0.0144
Zn2—S32—C31	83.61(8)	81.8	1.81	3.2761
Zn2—S41—C41	91.11(8)	94.03	2.92	8.5264
Zn1—S42—Zn2	86.21(2)	92.11	5.9	34.81
Zn1—S42—C41	98.63(8)	104.29	5.66	32.0356
Zn2—S42—C41	81.57(8)	78.59	2.98	8.8804
C11—N12—C111	121.1(2)	120.51	0.59	0.3481
C11—N12—C114	123.4(2)	123.19	0.21	0.0441
C111—N12—C114	115.4(2)	116.27	0.87	0.7569
C112—N13—C113	117.4(2)	117.63	0.23	0.0529
C112—N13—C121	121.3(2)	122.86	1.56	2.4336
C113—N13—C121	120.3(2)	119.35	0.95	0.9025
C21—N21—C211	125.5(2)	124.51	0.99	0.9801
Mean			3.614103	26.03925

Table S 3: Frontier molecular orbital reactivity parameters obtained from DFT

Property	**Value**
E_{HOMO}	-5.0014
E_{LUMO}	-1.2985
Energy gap ($\Delta E_{LUMO-HOMO}$)	3.7030
Ionization energy (IP = $-E_{HOMO}$)	5.0014
Electron affinity (EA = $-E_{LUMO}$)	1.2985
Global hardness (η = (IP-EA)/2)	1.85145
Global softness ($\sigma = 1/2\eta$)	0.54012
Chemical potential (μ = -(IP+EA)/2)	-3.14995
Electronegativity ($\chi = -\mu$)	3.14995
Electrophilicity index ($\omega = \mu^2/ 2\eta$)	2.67957
Nucleophilicity index ($N = 1/\omega$)	0.37319
Electron accepting power ($\omega^+ = (IP+EA)^2/8(IP-EA)$	1.33979
Electron donating power ($\omega^- = (IP-EA)^2/8(IP-EA)$	0.125