Supporting Information

Aggregation-Induced Enhanced Fluorescence Emission of Chiral Zn(II) complexes Coordinated by Schiff-Base Type Binaphthyl Ligands

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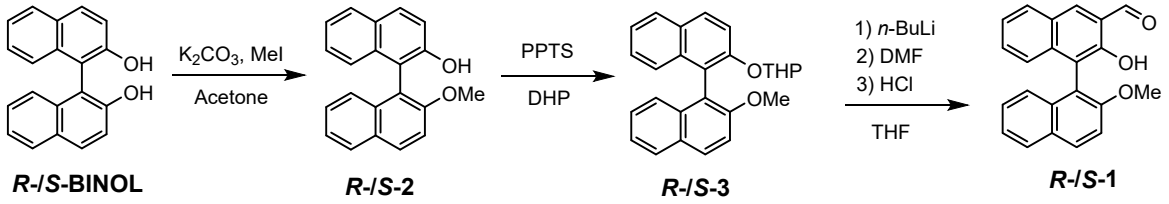
Synthetic procedure of the ligands

The Schiff-base type chiral ligands were synthesized from commercially available BINOL as shown in Scheme 1 according to the previous report.[1]

Scheme 1



***R*-/*S*-BINOL** ***R*-/*S*-2** ***R*-/*S*-3** ***R*-/*S*-1**

PPTS = pyridinium *p*-toluenesulfonate, DHP = 3,4-dihydro-2H-pyran

(*R*)-/(*S*) -2'-methoxy-[1,1'-binaphthalen]-2-ol (***R*-/*S*-2**)

***R*-2**: ^{1}H-NMR (500 MHz,$CDCl_3$): δ 8.07(1H, d), 7.92(2H, d), 7.86(1H, d), 7.50(1H, d), 7.39(2H, m), 7.30(2H, m), 7.21(1H, t), 7.17(1H, d), 7.05(1H, d), 4.93(1H, s), 3.82(3H, s)

***S*-2**: ^{1}H-NMR (500 MHz,$CDCl_3$): δ 8.07(1H, d), 7.92(2H, d), 7.86(1H, d), 7.50(1H, d), 7.40(2H, m), 7.30(2H, m), 7.21(1H, t), 7.17(1H, d), 7.05(1H, d), 4.95(1H, s), 3.83(3H, s)

(*R*)-/(*S*) -(2-(2'-methoxy-[1,1'-binaphthalen]-2-yl)oxy)tetrahydro-2H-pyran (***R*-/*S*-3**)

***R*-3**: ^{1}H-NMR (500 MHz,$CDCl_3$): δ 7.96(2H, m), 7.87(2H, t), 7.59(1H, dd), 7.44(1H, m), 7.33(2H, m), 7.21(4H, m), 3.76(3H, s), 1.15-1.58(8H, m).

***S*-3**: ^{1}H-NMR (500 MHz,$CDCl_3$): δ 7.96(2H, m), 7.87(2H, t), 7.59(1H, dd), 7.44(1H, m), 7.33(2H, m), 7.21(4H, m), 3.74(3H, s), 1.13-1.60(8H, m).

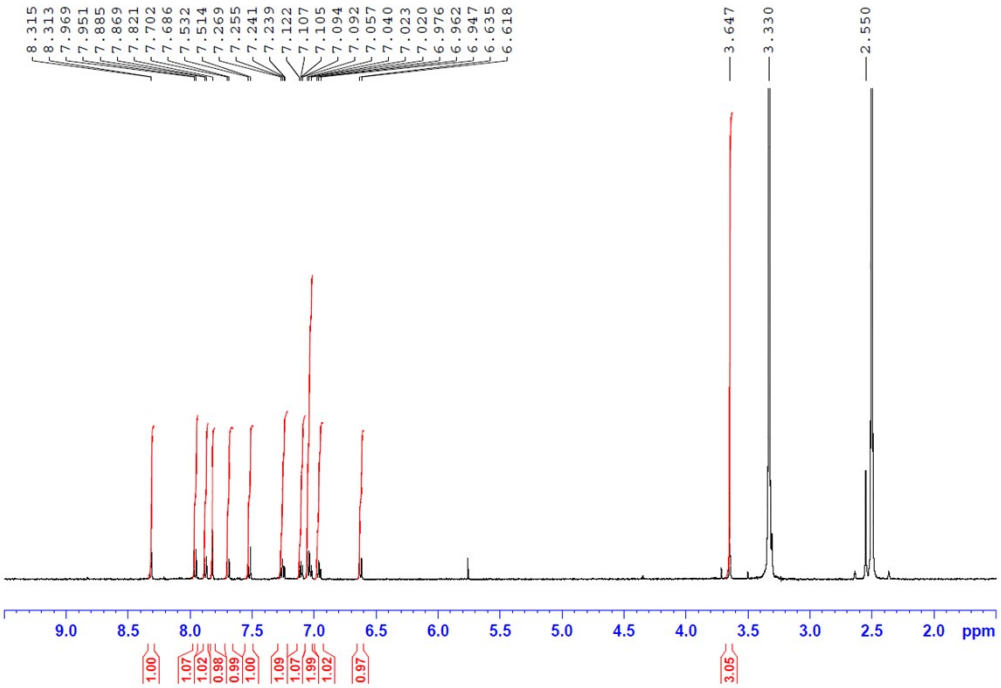
(*R*)-/(*S*) -2-hydroxy-2'-methoxy-[1,1'-binaphthalene]-3-carbaldehyde (***R*-/*S*-1**)

***R*-1**: ^{1}H-NMR (500 MHz,$CDCl_3$): δ10.47(1H, s), 10.19(1H, s), 8.32(1H, s), 8.03(1H, d), 7.99(1H, m), 7.89(1H, d), 7.49(1H, d), 7.38-7.33(3H, m), 7.26(1H, t), 7.17-7.12(2H, m), 3.81(3H, s)

***S*-1**: ^{1}H-NMR (500 MHz,$CDCl_3$): δ10.48(1H, s), 10.20(1H, s), 8.33(1H, s), 8.03(1H, d), 7.99(1H, m), 7.89(1H, d), 7.49(1H, d), 7.39-7.33(3H, m), 7.26(1H, t), 7.18-7.12(2H, m), 3.81(3H, s)

1. (a) L. Jin, Y. Huang, H. Jing, T. Chang and P. Yan, *Tetrahedron: Asymmetry*, 2008, **19**, 1947-1953; (b) F. Meng, Y. Li, W. Zhang, S. Li, Y. Quan and Y. Cheng, *Polym. Chem*., 2017, **8**, 1555-1561.

(a)



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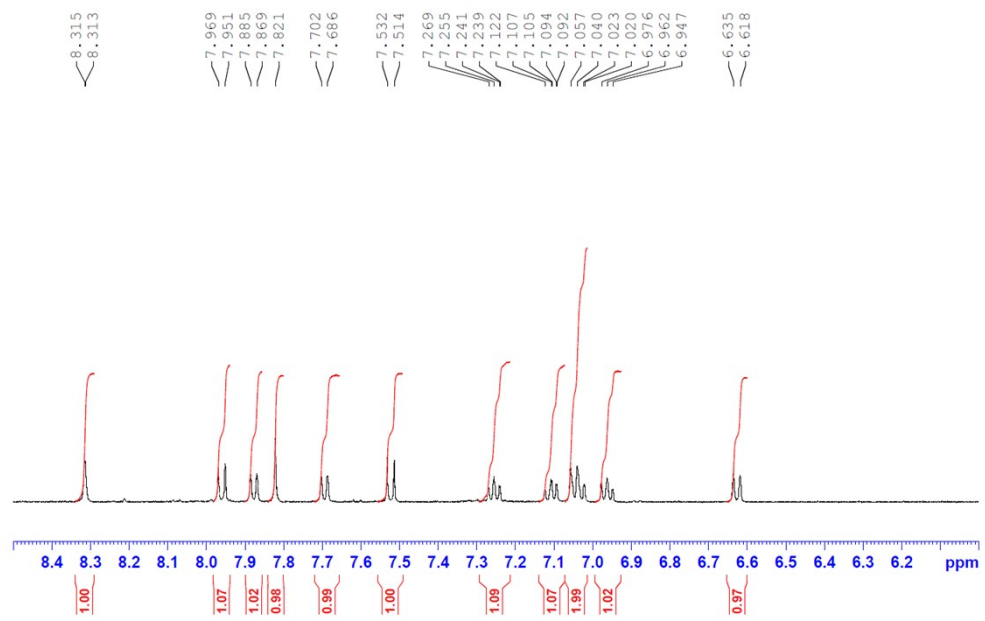
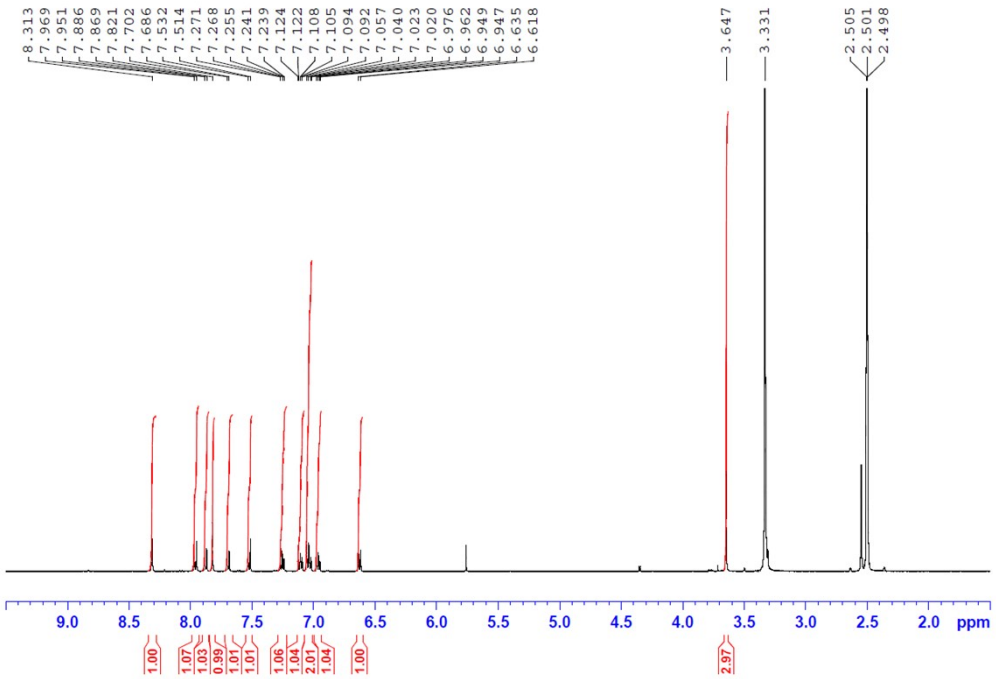


Figure S1. (a) ^{1}H-NMR spectrum of ***R*-Zn** (500 MHz, d_6-DMSO, 298 K, Me_4Si) and (b) expanded NMR spectrum of ***R*-Zn**.

(a)



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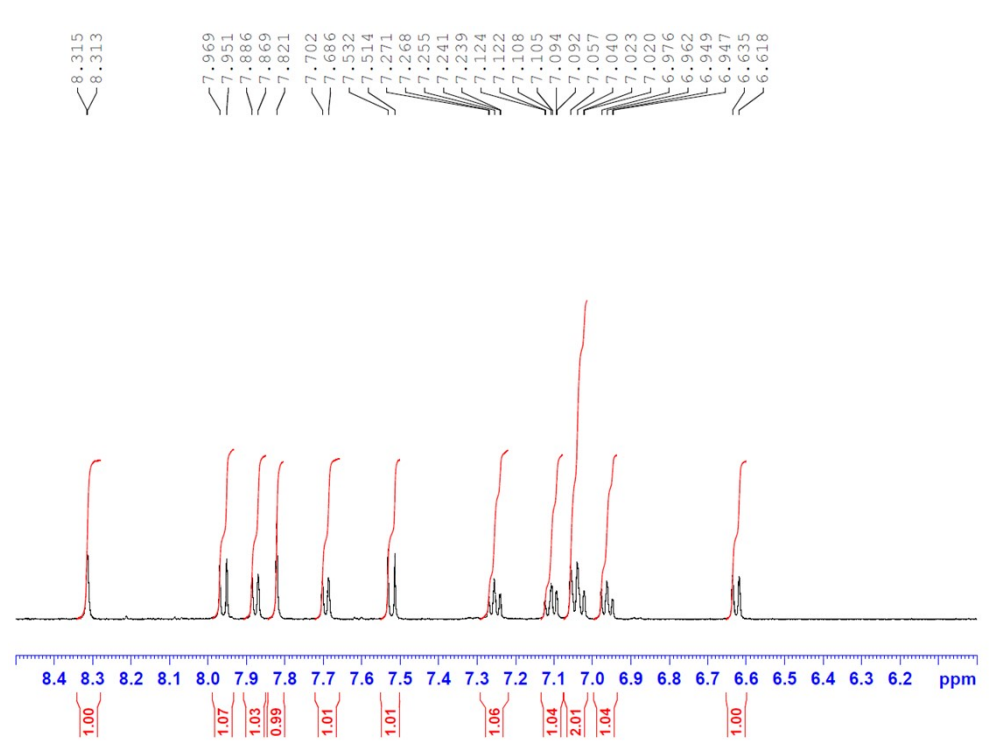


Figure S2. (a) ^{1}H-NMR spectrum of ***S*-Zn** (500 MHz, d_6-DMSO, 298 K, Me_4Si) and (b) expanded NMR spectrum of ***S*-Zn**.

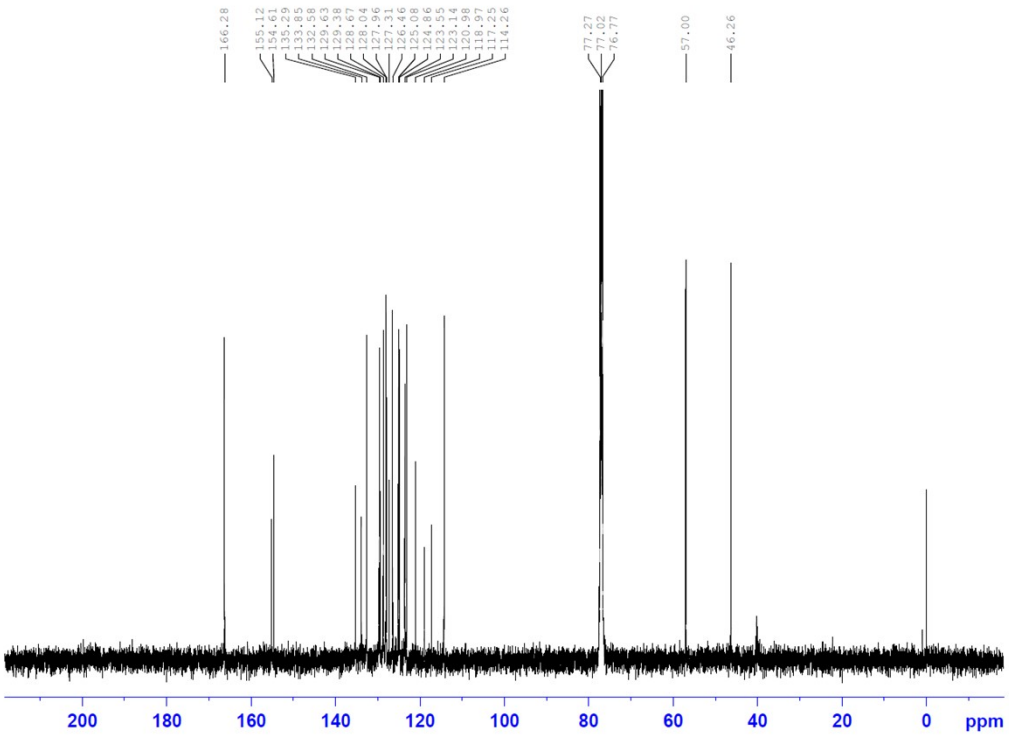


Figure S3. ^{13}C-NMR spectrum of ***R*-Zn** (500 MHz, *d*-chloroform, 298 K, Me_4Si).

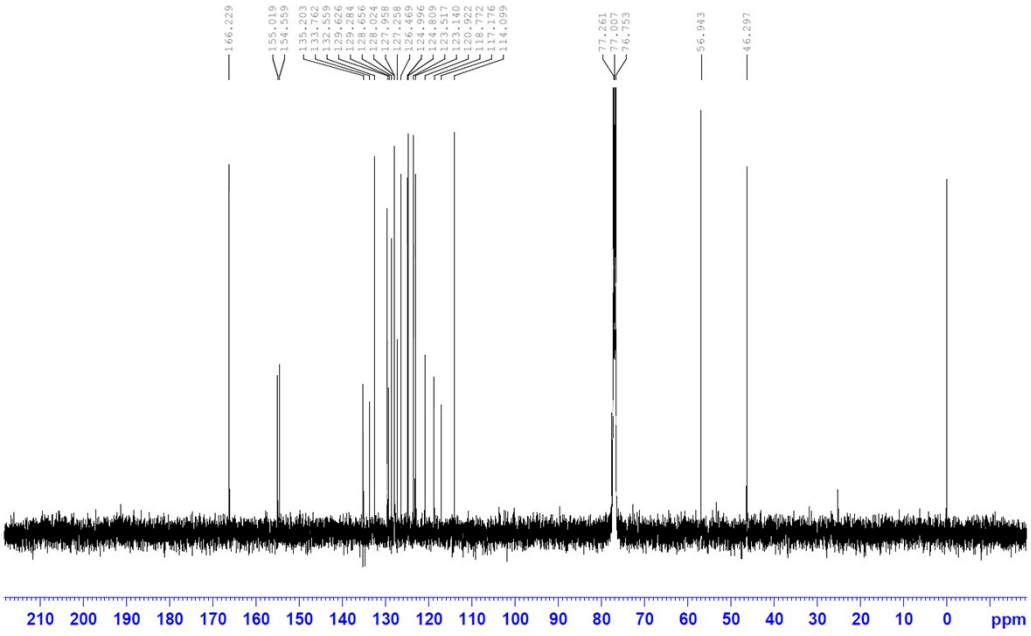


Figure S4. ^{13}C-NMR spectrum of ***S*-Zn** (500 MHz, *d*-chloroform, 298 K, Me_4Si).

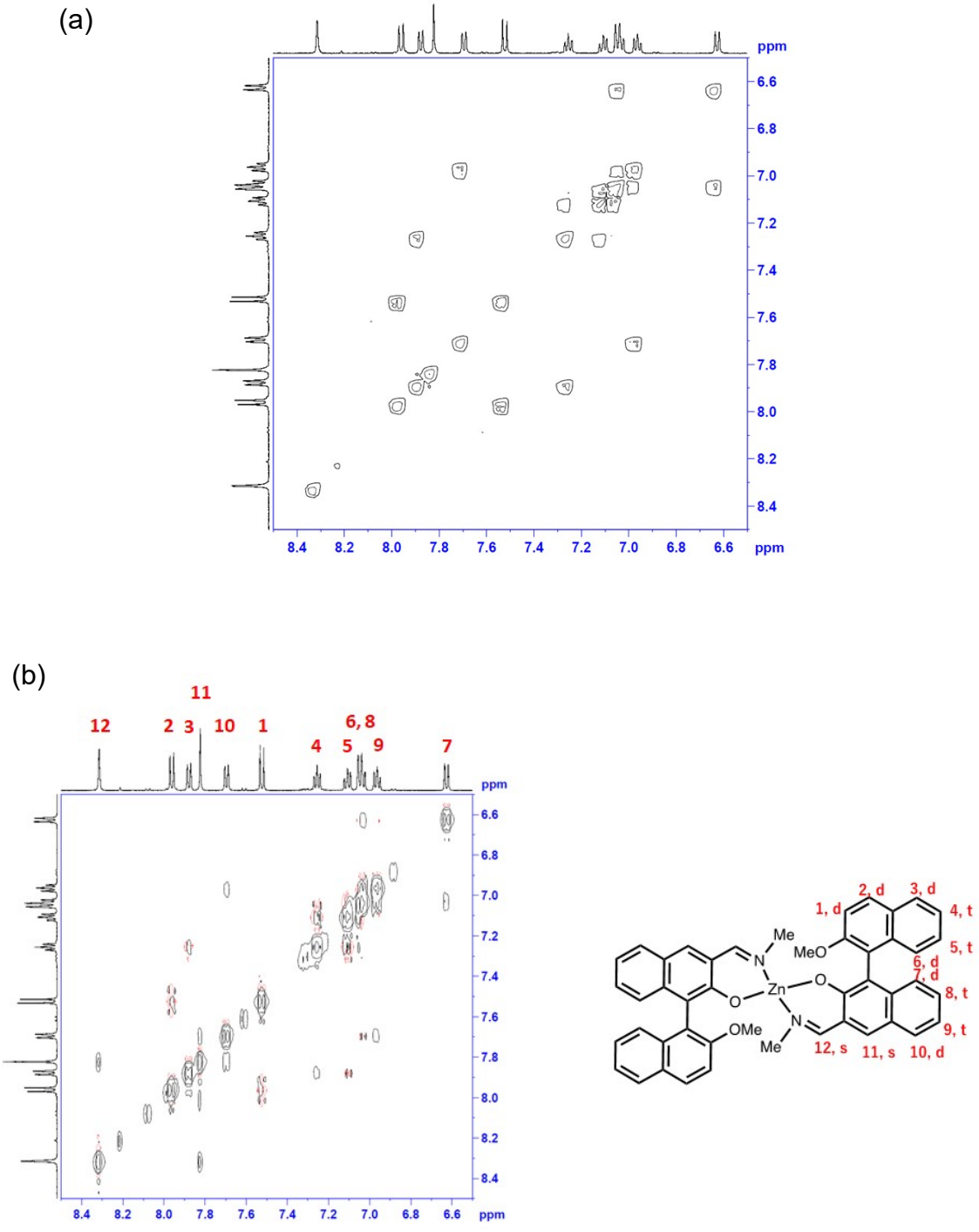
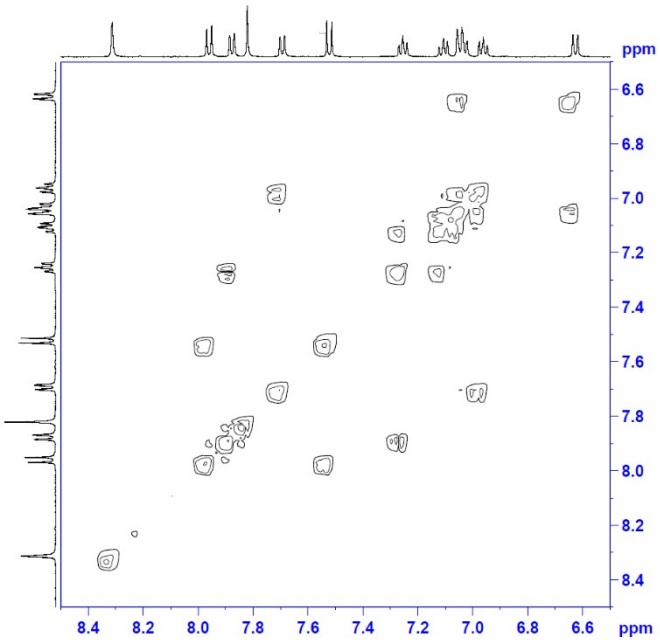
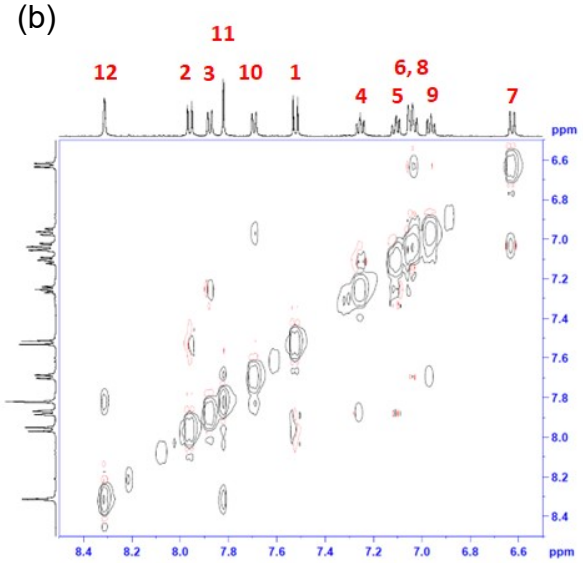


Figure S5. (a) COSY and (b) NOESY spectra of ***R*-Zn** (500 MHz, d_6-DMSO, 298 K, Me_4Si).

(a)



(b)



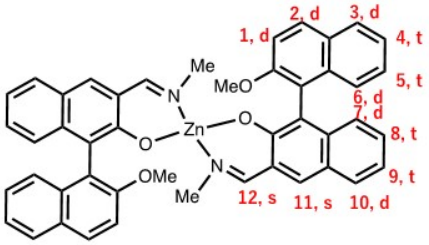


Figure S6. (a) COSY and (b) NOESYspectrum of ***S*-Zn** (500 MHz, d_6-DMSO, 298 K, Me_4Si).

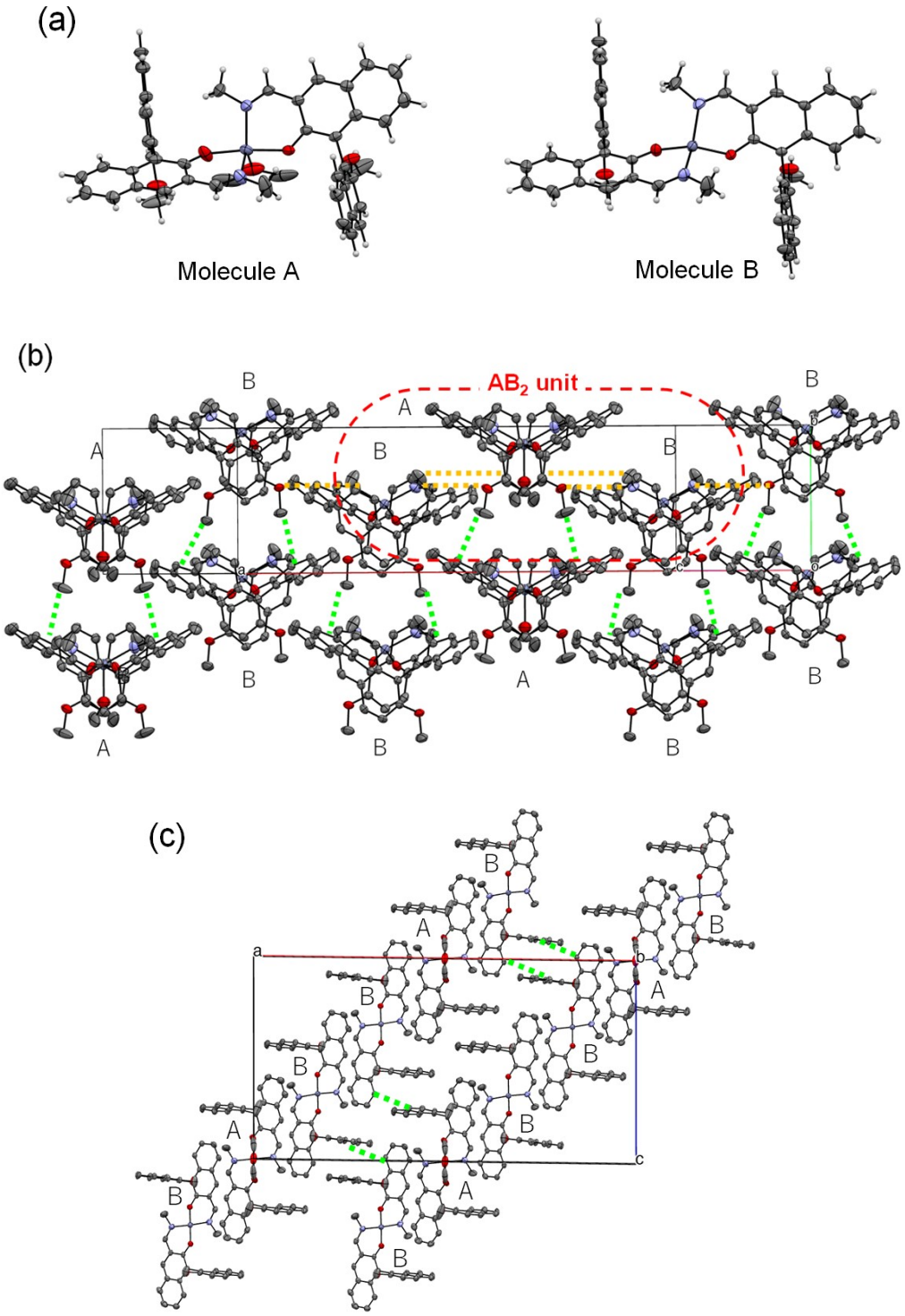


Figure S7. Crystal structure of ***S*-Zn**. (a) Molecular structure of ***S*-Zn**; Molecule A (left) and molecule B (right); (b) crystal structure of ***S*-Zn** (green dotted line : CH…π interactions, orange dotted line : CH…O interactions); (c) crystal structure of ***S*-Zn** projected along *b*-axis.

Table S1. Crystallographic data for ***R*-Zn** and ***S*-Zn**.

	***R*-Zn**	***S*-Zn**
Formula	$C_{69.5}H_{54}N_3O_8Zn_{1.5}$	$C_{69.5}H_{54}N_3O_8Zn_{1.5}$
Formula weight	1157.21	1157.21
Color	Yellow	Yellow
Crystal size/ mm	0.330 × 0.170 × 0.090	0.240 × 0.210 × 0.060
Crystal system	Monoclinic	Monoclinic
Space group	*C*2	*C*2
a (Å)	35.6573(7)	35.7404(7)
b (Å)	8.2326(2)	8.2238(2)
c (Å)	18.9983(4)	18.9816(4)
β / °	90.879(2)	90.815(2)
V(Å ^{3})	5576.3(2)	5578.5(2)
Z	4	4
F(000)	2404	2404
D_{calc} (g/cm^3)	1.378	1.378
Abs coeff (mm^{-1})	0.713	0.713
Flack parameter	-0.004(3)	-0.003(4)
R_1[a] ($I > 2\sigma(I)$)	0.0415	0.0403
R_w[b] ($I > 2\sigma(I)$)	0.0964	0.0952
R_1[a] (all data)	0.0484	0.0464
R_w[b] (all data)	0.0996	0.0979

[a] $R_1 = \sum \left| |F_0| - |F_c| \right| / \sum |F_0|$ *for* $I > 2\sigma(I)$ data

[b] $R_w = \left\{ \sum w \left(|F_0| - |F_c| \right)^2 / \sum w |F_0|^2 \right\}^{1/2}$

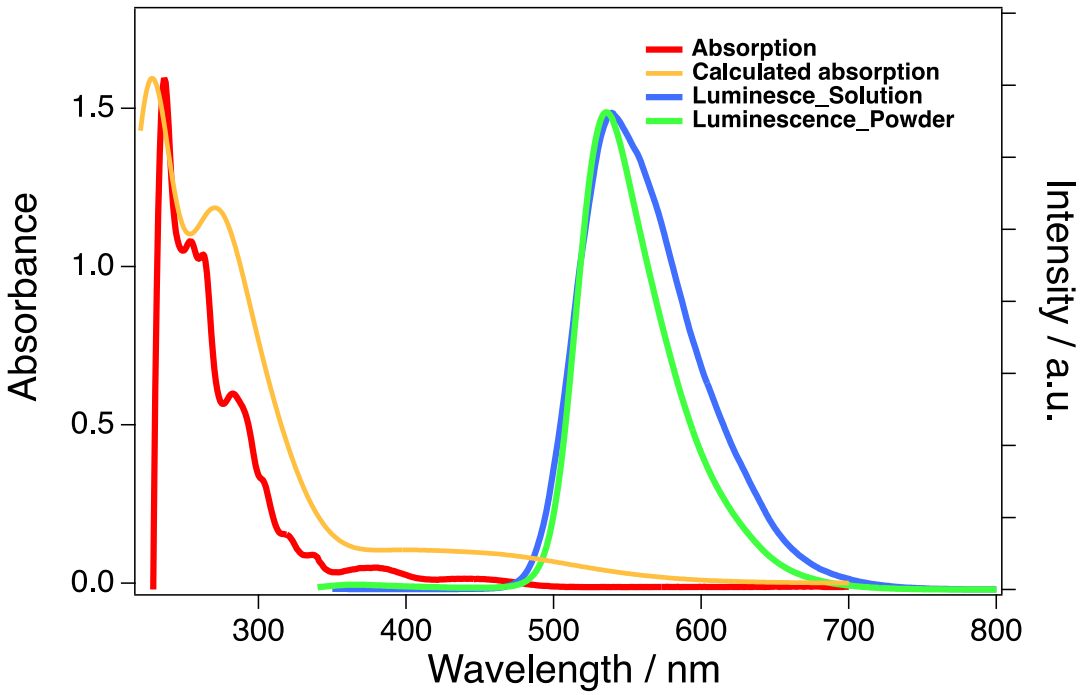


Figure S8. Absorption spectrum of ***S*-Zn** (red, 1.0×10^{-5} M in CH_2Cl_2), the calculated spectrum (orange), and emission spectra in 1.0×10^{-4} M CH_2Cl_2 solution (blue) and in powder (green) excited at 300 nm.

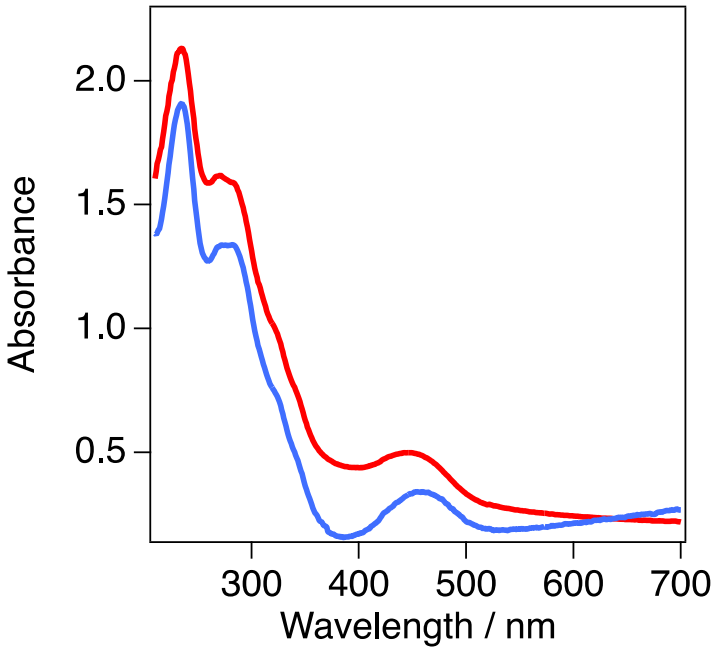


Figure S9. Absorption spectra of ***R*-Zn**(red) and ***S*-Zn**(blue) in 0.1 wt% KBr pellet.

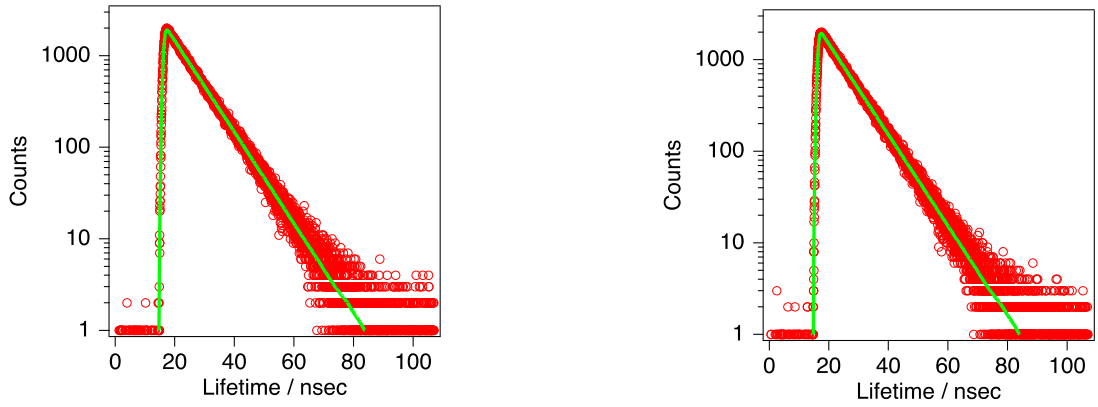


Figure S10. Emission decay profiles of ***R*-Zn** (left) and ***S*-Zn** (right) in CH_2Cl_2 solutions excited at 370 nm and fit (green solid line).

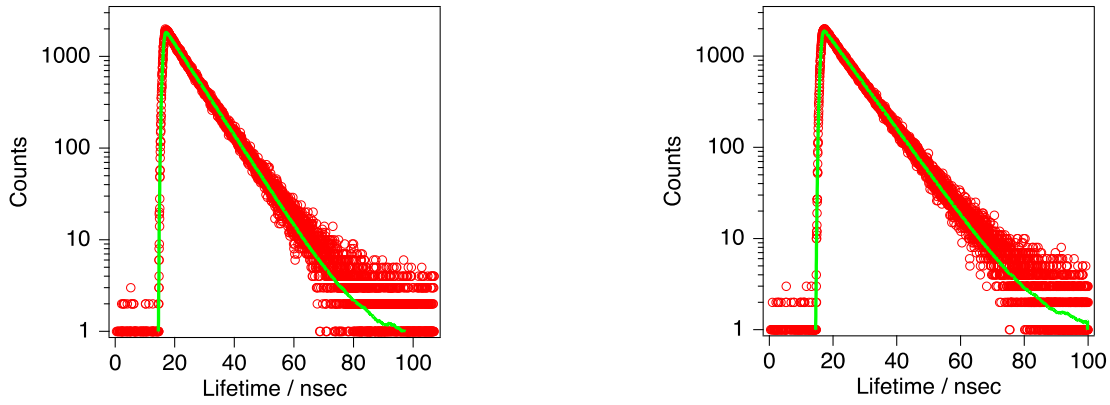


Figure S11. Emission decay profiles of ***R*-Zn** (left) and ***S*-Zn** (right) in powders excited at 370 nm and fit (green solid line).

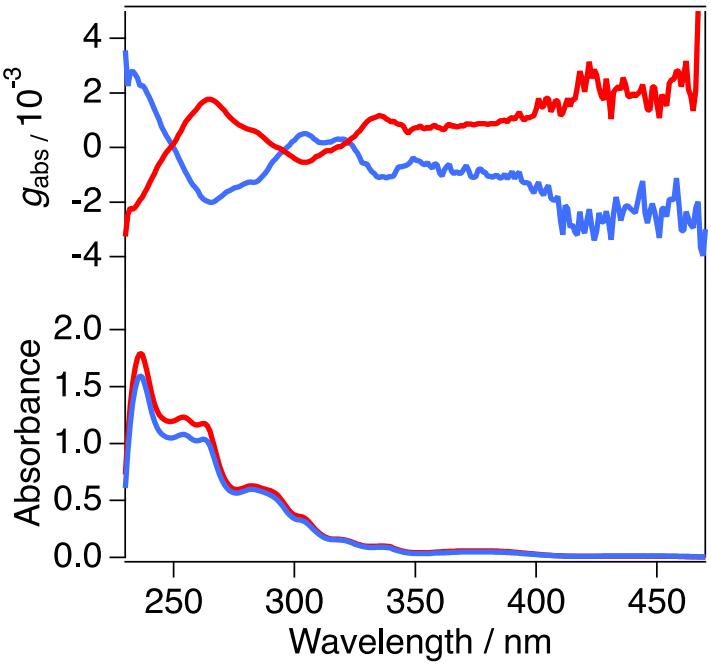


Figure S12. CD spectra (upper) and UV-vis spectra (lower) of ***R*-Zn** (red) and ***S*-Zn** (blue) in 10^{-5} M CH_2Cl_2 solution.

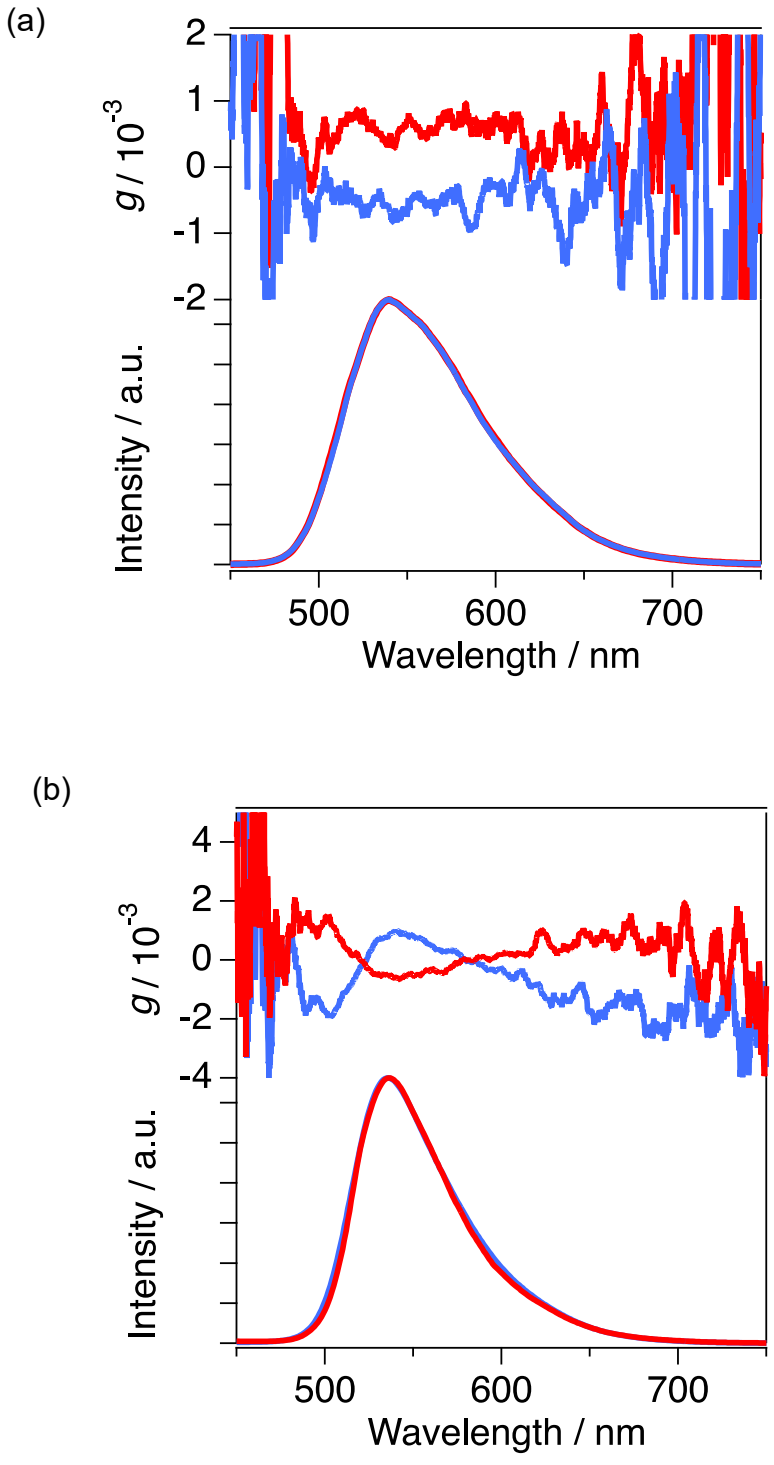


Figure S13. (a) CPL spectra (upper) and emission spectra (lower) of ***R*-Zn** (red) and ***S*-Zn** (blue) in CH_2Cl_2 solution; (b) CPL spectra (upper) and emission spectra (lower) of ***R*-Zn** (red) and ***S*-Zn** (blue) in powders.

Table S2. Spectroscopic data of CH_2Cl_2 solutions and powder samples of ***R*-Zn** and ***S*-Zn**.

	Sample	***R*-Zn**	***S*-Zn**
Quantum yield	CH_2Cl_2 soln. (λ_{ex} = 300 nm)	11.9%	12.0%
	Powder (λ_{ex} = 300 nm)	26.2%	25.1%
Lifetime / ns	CH_2Cl_2 soln. (λ_{ex} = 300 nm, λ_{det} = 540 nm)	8.7	8.7
	Powder (λ_{ex} = 300 nm, λ_{det} = 540 nm)	8.7	9.1
k_f / ns^{-1}	CH_2Cl_2 solution	0.0137	0.0138
	Powder	0.0301	0.0276
k_{nr} / ns^{-1}	CH_2Cl_2 solution	0.101	0.101
	Powder	0.0848	0.0823
g_{abs}	CH_2Cl_2 solution	1.8×10^{-3}	2.0×10^{-3}
g_{cpl}	CH_2Cl_2 soln. (λ_{ex} = 300 nm)	0.86×10^{-3}	-0.62×10^{-3}
	Powder (λ_{ex} = 300 nm)	-0.84×10^{-3}	1.0×10^{-3}

$k_f = \Phi/\tau$, $k_{nr} = (1-\Phi)/\tau$

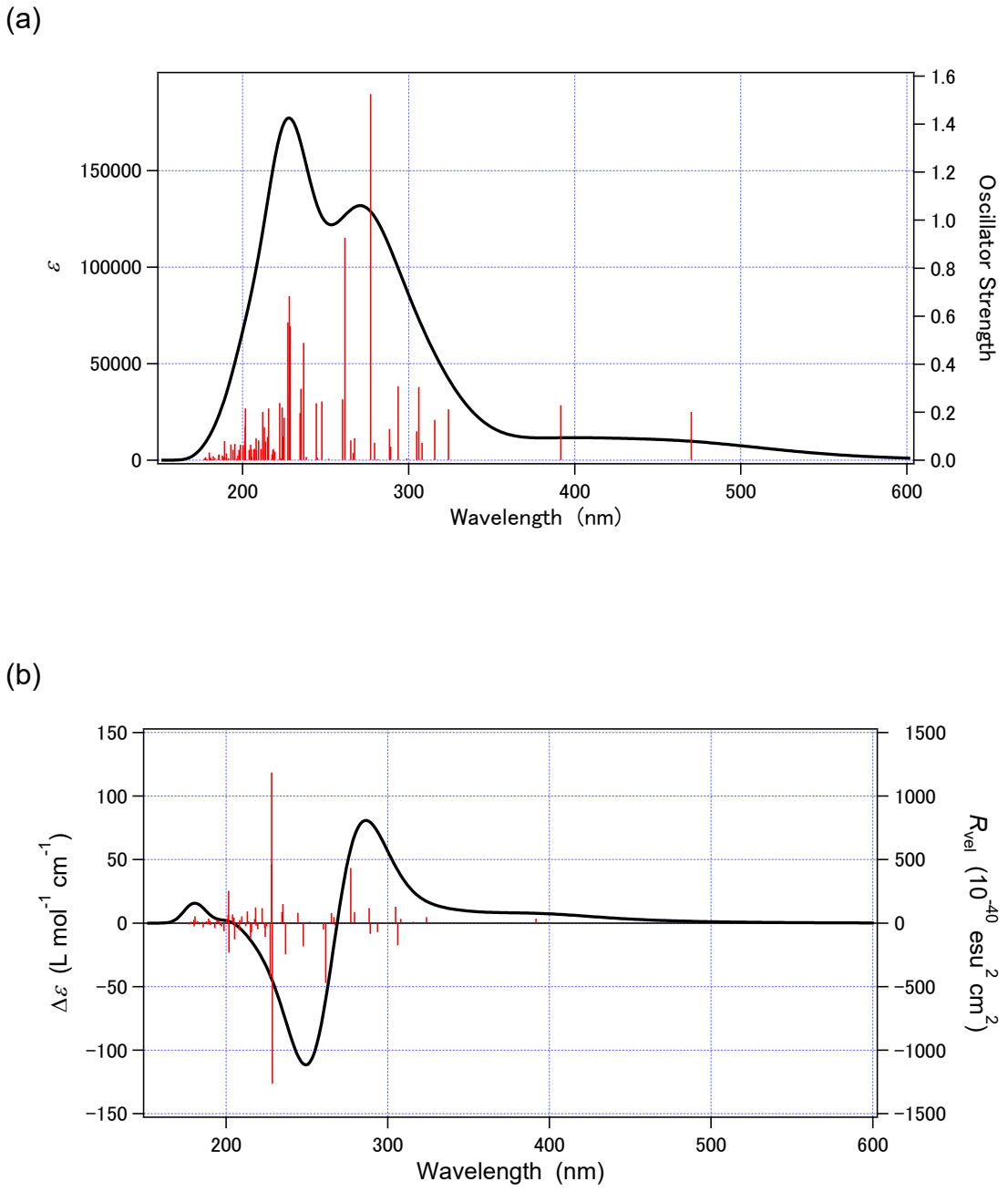


Figure S14. Simulated (a) UV-vis and (b) CD spectra of ***R*-Zn** from TD-DFT calculations.

Table S3. Selected excitation energies and main weights of transition for ***R*-Zn** calculated by TD-DFT method.

Excited state	Experiment (nm)	Excitation Energy (nm) (Oscillator strength, R_{vel})	Transitions (% weight)
1	430-473 (broad)	470 (0.2013, 5.2199)	194 → 195 (47.9)
2	379	392 (0.2292, 35.0748)	193 → 196 (46.5)
14	282	277 (1.5248, 433.2627)	194 → 200 (30.2) 194 → 199 (7.5) 189 → 195 (4.9)
18	250-263	262 (0.9268, –470.5516)	193 → 199 (22.1) 190 → 196 (6.1) 193 → 200 (4.4)
30	236	228 (0.6831, 1186.6658)	191 → 201 (10.6) 190 → 195 (6.2) 193 → 201 (5.6)

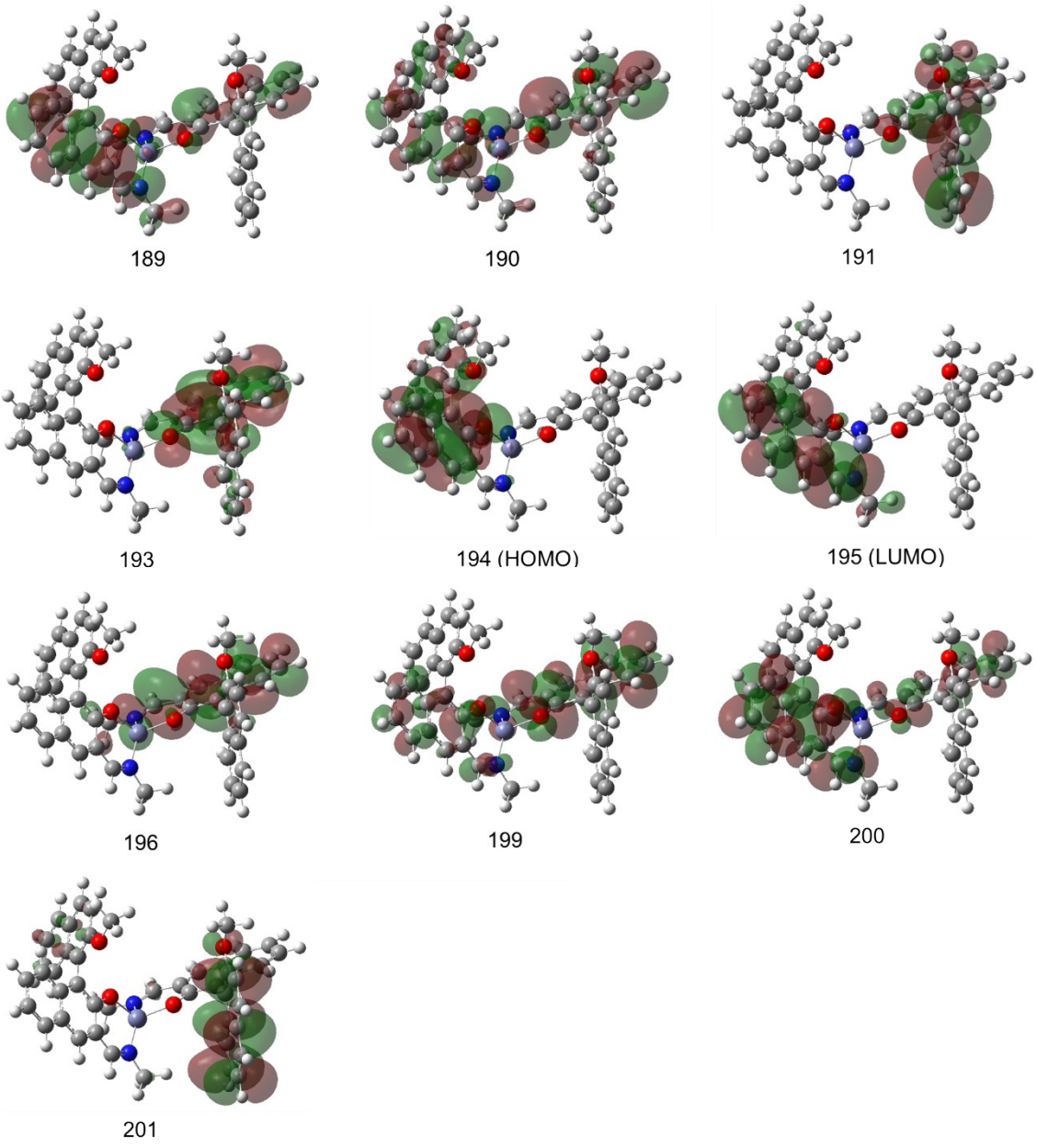


Figure S15. Molecular orbitals of ***R*-Zn** related to the excitation listed in Table S3.

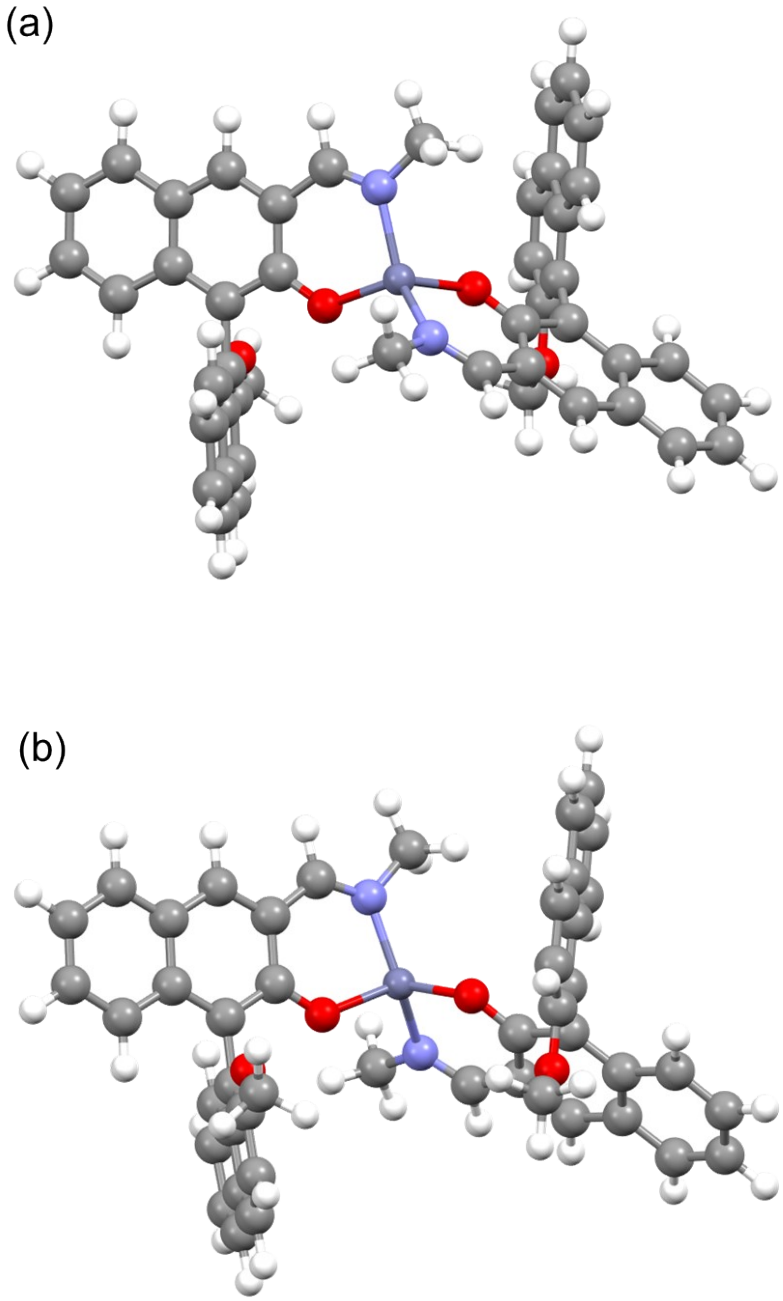


Figure S16. Optimized molecular structures of (a) ***R*-Zn** and (b) ***S*-Zn**

Table S4. Cartesian coordinates of the optimized equilibrium structure of ***R*-Zn** calculated by DFT method (total energy: –3961.78619128 a.u.).

Atom	x	y	z
Zn	0.020188	-0.121184	-1.872875
O	1.561358	-0.167426	-0.724837
O	3.222343	0.263139	2.901076
N	0.345237	1.743876	-2.548143
C	-0.628784	2.354383	-3.430651
H	-1.607473	2.385132	-2.9291
H	-0.34237	3.378519	-3.718545
H	-0.740699	1.742727	-4.339079
C	1.37007	2.417906	-2.177283
H	1.474662	3.444439	-2.564108
C	2.446732	1.998552	-1.295496
C	3.468216	2.919066	-1.118727
H	3.406003	3.883208	-1.630896
C	4.583844	2.65616	-0.307534
C	5.629775	3.608687	-0.142268
H	5.54558	4.566907	-0.661671
C	6.714113	3.332313	0.645193
H	7.513799	4.065451	0.769093
C	6.796706	2.075568	1.302659
H	7.666574	1.853706	1.925885
C	5.806748	1.139162	1.165977
H	5.891269	0.178675	1.675223
C	4.655637	1.392414	0.358345
C	3.612559	0.449079	0.200529
C	2.495598	0.71871	-0.614134
C	3.648697	-0.861842	0.903498
C	3.873576	-2.07584	0.190656
C	4.105629	-2.092701	-1.21472

H	4.119142	-1.145711	-1.754861
C	4.310783	-3.271028	-1.88564
H	4.487477	-3.258394	-2.963854
C	4.299211	-4.5084	-1.193929
H	4.462633	-5.439216	-1.741486
C	4.08685	-4.527399	0.159743
H	4.078449	-5.472194	0.709253
C	3.870851	-3.322178	0.883013
C	3.650996	-3.323195	2.281547
H	3.648782	-4.27571	2.81679
C	3.440867	-2.153559	2.965291
H	3.270952	-2.181262	4.040797
C	3.434631	-0.915284	2.273514
C	3.016598	0.291627	4.2921
H	2.876381	1.345752	4.564122
H	2.115898	-0.272325	4.587504
H	3.885248	-0.103114	4.84548
O	-1.640661	0.046028	-0.77995
O	-3.241399	-0.209853	2.9037
N	-0.494022	-1.848341	-2.644218
C	0.413397	-2.519687	-3.546784
H	1.397349	-2.670283	-3.070321
H	0.030314	-3.50586	-3.858316
H	0.583514	-1.916397	-4.454988
C	-1.576919	-2.488323	-2.250153
H	-1.73344	-3.494254	-2.668759
C	-2.591428	-2.069702	-1.349163
C	-3.659904	-2.928408	-1.070482
H	-3.678504	-3.909952	-1.552602
C	-4.734003	-2.607082	-0.197846
C	-5.789255	-3.502637	0.045211

H	-5.773111	-4.482617	-0.437447
C	-6.851368	-3.157264	0.885069
H	-7.656515	-3.87684	1.052383
C	-6.89484	-1.90607	1.501336
H	-7.730914	-1.635092	2.148137
C	-5.855368	-0.998381	1.27769
H	-5.886393	-0.014019	1.746578
C	-4.765648	-1.323122	0.455037
C	-3.681685	-0.425014	0.216414
C	-2.595277	-0.775771	-0.656259
C	-3.608961	0.89147	0.881178
C	-3.743072	2.102355	0.134151
C	-4.046464	2.103306	-1.256104
H	-4.191475	1.150199	-1.76667
C	-4.167923	3.278221	-1.954685
H	-4.403218	3.25292	-3.021229
C	-3.998309	4.525381	-1.305206
H	-4.094631	5.452678	-1.874016
C	-3.727408	4.559814	0.038299
H	-3.606946	5.513493	0.558285
C	-3.601838	3.359703	0.789412
C	-3.348859	3.377804	2.182626
H	-3.238175	4.34049	2.687117
C	-3.244686	2.214334	2.900879
H	-3.04597	2.256765	3.970727
C	-3.372774	0.961675	2.250943
C	-3.018282	-0.223533	4.29457
H	-2.968931	-1.279353	4.589283
H	-2.066094	0.264148	4.561118
H	-3.840603	0.261435	4.846119

Table S5. Cartesian coordinates of the optimized equilibrium structure of ***S*-Zn** calculated by DFT method (total energy: –3961.78619127 a.u.).

Atom	x	y	z
Zn	0.020167	0.121169	-1.872797
O	-1.640692	-0.046026	-0.779882
O	1.561344	0.167374	-0.724762
O	-3.241457	0.209783	2.90376
O	3.22259	-0.26312	2.901065
N	0.345185	-1.743897	-2.548069
N	-0.494013	1.848341	-2.644126
C	3.441119	2.153579	2.965218
H	3.271287	2.181302	4.040737
C	3.651191	3.323204	2.281438
H	3.649018	4.275728	2.816663
C	3.870939	3.322161	0.882887
C	4.086879	4.527369	0.159578
H	4.078518	5.472174	0.709073
C	4.299138	4.508347	-1.19411
H	4.462515	5.439154	-1.741695
C	4.310662	3.270963	-1.885798
H	4.487276	3.258309	-2.964025
C	4.105561	2.092647	-1.214842
H	4.119035	1.145647	-1.754967
C	3.873613	2.07581	0.190552
C	3.648789	0.861824	0.903433
C	3.434829	0.915291	2.273465
C	3.016989	-0.291587	4.292111
H	2.876801	-1.345708	4.564163
H	3.885697	0.103163	4.845394
H	2.116319	0.272369	4.587601
C	3.612605	-0.44911	0.200488
C	4.65569	-1.392446	0.358261

C	5.806845	-1.139187	1.165829
H	5.891398	-0.178692	1.675054
C	6.796804	-2.075596	1.302475
H	7.666706	-1.853729	1.925654
C	6.714171	-3.332351	0.645034
H	7.513859	-4.065492	0.768907
C	5.629793	-3.60873	-0.142369
H	5.545566	-4.566957	-0.661755
C	4.583859	-2.6562	-0.307598
C	3.468194	-2.91911	-1.11874
H	3.405958	-3.883254	-1.630901
C	2.446706	-1.998594	-1.29547
C	2.495599	-0.718751	-0.614111
C	1.370014	-2.417941	-2.177223
H	1.474581	-3.444479	-2.564042
C	-0.628863	-2.354396	-3.430553
H	-0.740789	-1.742742	-4.338981
H	-0.342468	-3.378536	-3.718449
H	-1.607542	-2.38513	-2.928982
C	-1.576884	2.488351	-2.250036
H	-1.733374	3.494297	-2.668619
C	-2.591401	2.069743	-1.34905
C	-3.659849	2.928477	-1.070346
H	-3.678415	3.910035	-1.552438
C	-4.73396	2.607159	-0.197724
C	-5.789185	3.502742	0.045356
H	-5.773006	4.482737	-0.437271
C	-6.851314	3.157376	0.885196
H	-7.656439	3.876973	1.052528
C	-6.894832	1.906164	1.501421
H	-7.730919	1.635191	2.148207
C	-5.855388	0.998448	1.277753

H	-5.886449	0.014071	1.746609
C	-4.76565	1.32318	0.455119
C	-3.681714	0.425045	0.216476
C	-2.595289	0.775795	-0.656179
C	-3.60904	-0.891461	0.8812
C	-3.372872	-0.961719	2.250965
C	-3.743192	-2.102317	0.134133
C	-4.046568	-2.103212	-1.256126
H	-4.191533	-1.150083	-1.766663
C	-4.168068	-3.2781	-1.954745
H	-4.403349	-3.252756	-3.021291
C	-3.998513	-4.525288	-1.305303
H	-4.094867	-5.452563	-1.874143
C	-3.727629	-4.559774	0.038204
H	-3.607213	-5.513474	0.558161
C	-3.602017	-3.359692	0.789356
C	-3.349056	-3.377847	2.182572
H	-3.238418	-4.340552	2.687035
C	-3.244843	-2.214404	2.900863
H	-3.046143	-2.256877	3.970712
C	-3.018369	0.22341	4.294635
H	-2.968977	1.279219	4.589383
H	-3.840723	-0.261539	4.846151
H	-2.066209	-0.264322	4.561189
C	0.413427	2.519681	-3.546676
H	0.583552	1.916392	-4.454878
H	0.030357	3.505858	-3.858212
H	1.397372	2.670269	-3.070197