Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Highly sensitive Ru(II) complex-based phosphorescent probe for thiophenol detection with aggregation-induced emission characteristics

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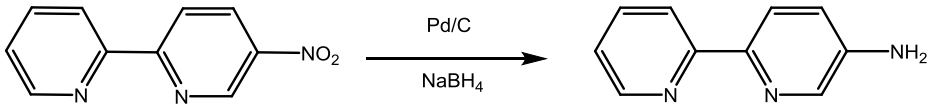
1. Synthesis and characterization

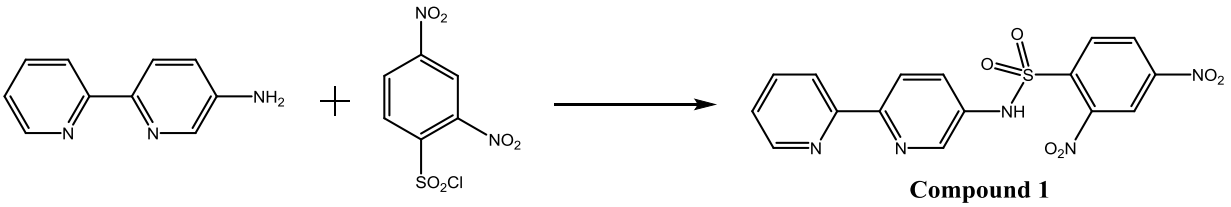
5-nitro-2,2'-bipyridine[S1] and cis-$Ru(bpy)_2Cl_2$[S2] were synthesized according to the previously published method.

1.1 Synthesis of 5-amine-2,2'-bipyridine



5-nitro-2,2'-bipyridine(0.5g, 2.48mmol) was dissolved in 100 ml methanol, and Pd/C (10%, 0.12g) was added. The mixture was stirred in an ice-cooled water bath, and then $NaBH_4$(1.5g) was gradually added to the solution. After stirring at room temperature for 5h, the mixture was filtrated and water (100ml) was added to the filtrate. The solution was extracted with CH_2Cl_2, and dried with anhydrous Na_2SO_4, and further concentrated under reduced pressure. 5-amine-2,2'-bipyridine was produced as a yellow solid (0.3g, % yield) which was used for the subsequent synthesis without further purification. ^{1}H NMR (400 MHz, DMSO) δ 8.54 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.18 (dt, J = 8.1, 1.0 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 8.02 (d, J = 2.7 Hz, 1H), 7.87 – 7.75 (m, 1H), 7.25 (ddd, J = 7.4, 4.8, 1.2 Hz, 1H), 7.02 (dd, J = 8.6, 2.8 Hz, 1H), 5.68 (s, 2H).

1.2 Synthesis of compound 1



Compound 1

5 mL dichloromethane solution of 2,4-dinitrobenzenesulfonyl chloride (128 mg, 0.48 mmol) was slowly added to the 10 ml dichloromethane solution of compound 1 (68 mg, 0.4 mmol) and Cs_2CO_3(130mg, 0.4mmol) was added to the solution. The mixture was reacted for 12 h at room temperature and the final product compound 2 (90mg, 56.2 %) was obtained by column chromatography over silica gel column using dichloromethane/methanol (5:1) as eluent. ^{1}H NMR (400 MHz, DMSO) δ 8.60 (d, J = 2.1 Hz, 1H), 8.53 (d, J = 3.6 Hz, 1H), 8.39 (dd, J = 8.6, 2.2 Hz, 1H), 8.19 (s, 1H), 8.12 (d, J = 8.7 Hz, 1H), 8.08 – 7.98 (m, 2H), 7.81 (s, 1H), 7.27 (d, J = 6.2 Hz, 2H). HRMS (ESI) m/z: calcd for $C_{16}H_{11}N_5O_6S$, $[M + Na]^+$, 424.0327; found, 424.0322.

References

[S1] L. Yang, X. Jing, C. He, Z. Chang, C. Duan, Redox-Active M8L6 Cubic Hosts with Tetraphenylethylene Faces Encapsulate Organic Dyes for Light‐Driven H2 Production. Chem. Eur. J., 2016, 22, 18107-18114.

[S2] B. P. Sullivan, D. J. Salmon, T. J. Meyer, Mixed phosphine 2, 2'-bipyridine complexes of ruthenium. Inorg. Chem., 1978, 17, 3334-3341.

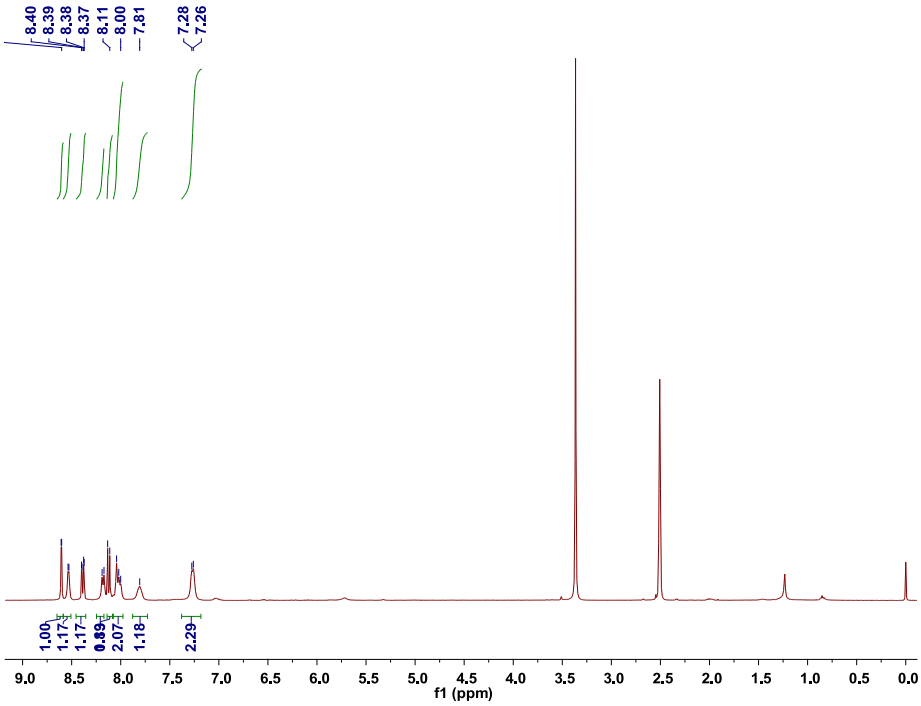


Figure S1. ^{1}H NMR spectrum of **compound 1** in d^{6}-DMSO.

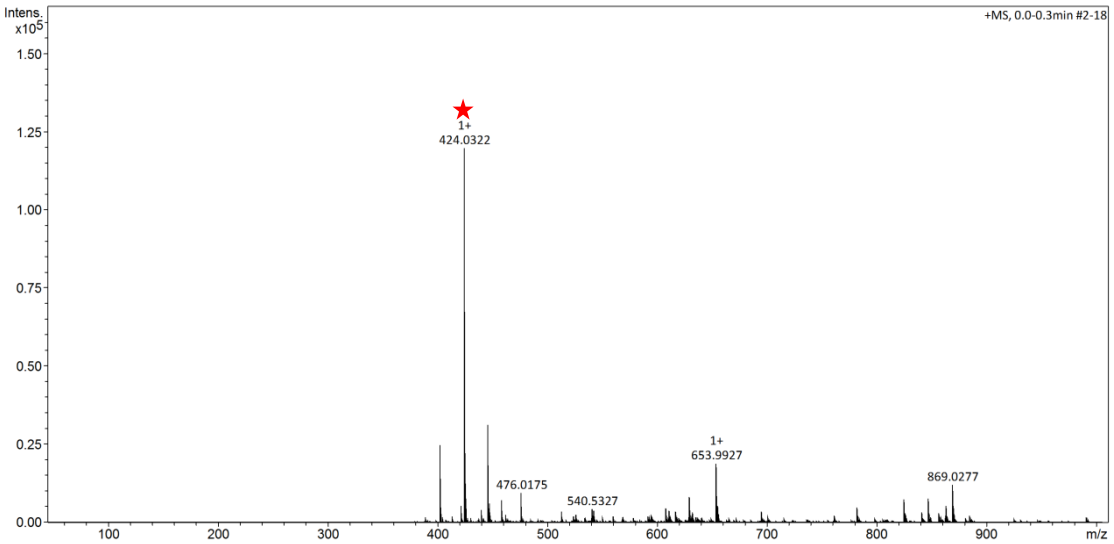


Figure S2. HRMS spectra of **compound 1**

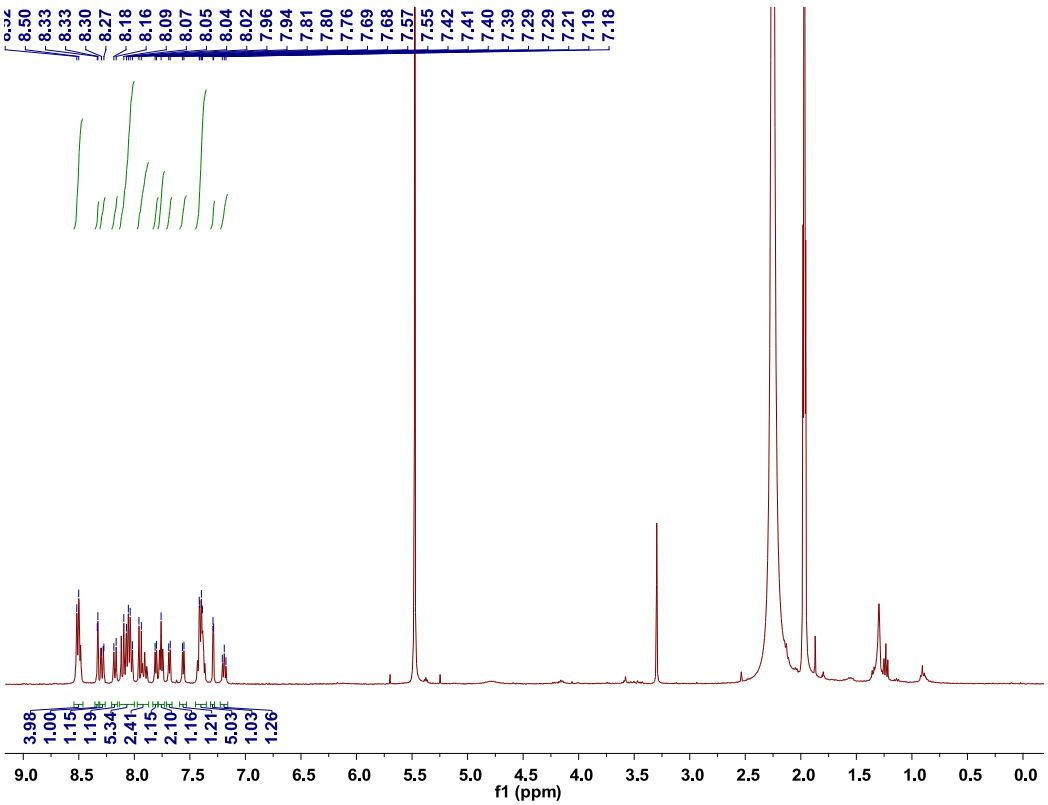


Figure S3. ^{1}H NMR spectrum of probe **Ru-LYP** in CD_3CN.

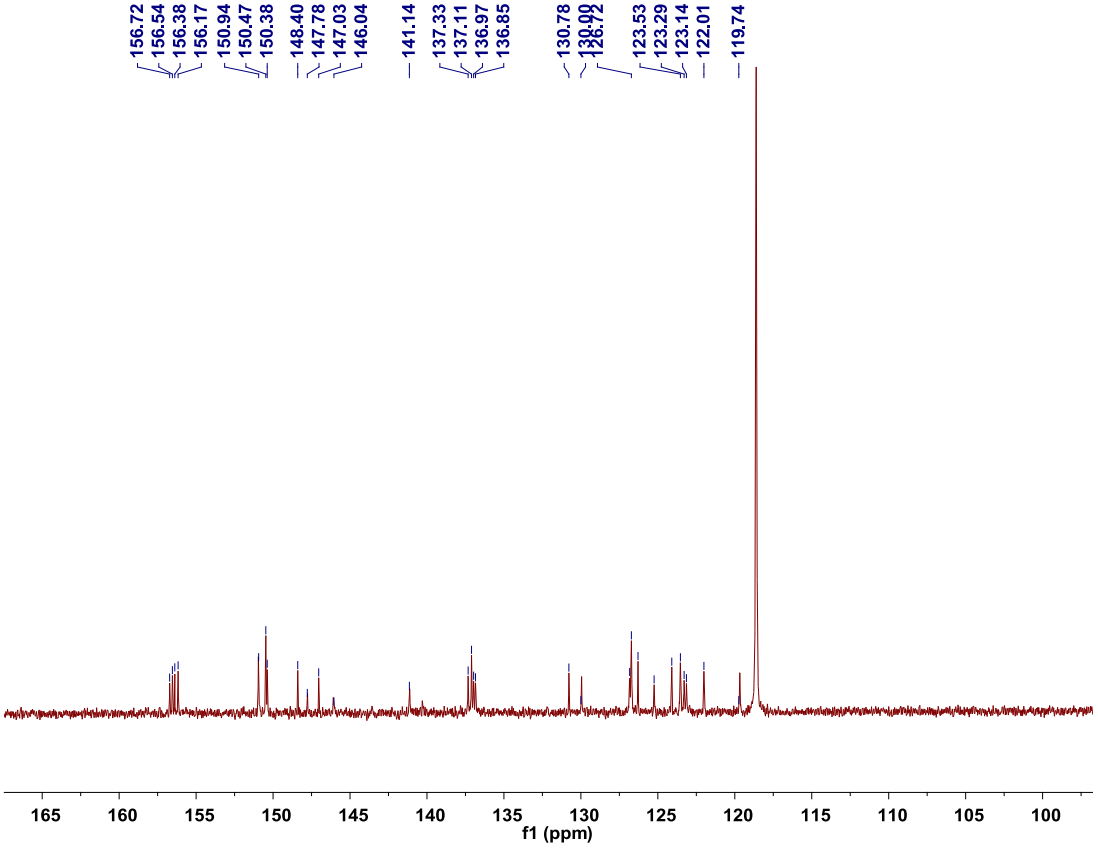


Figure S4. ^{13}C NMR spectrum of probe **Ru-LYP** in CD_3CN.

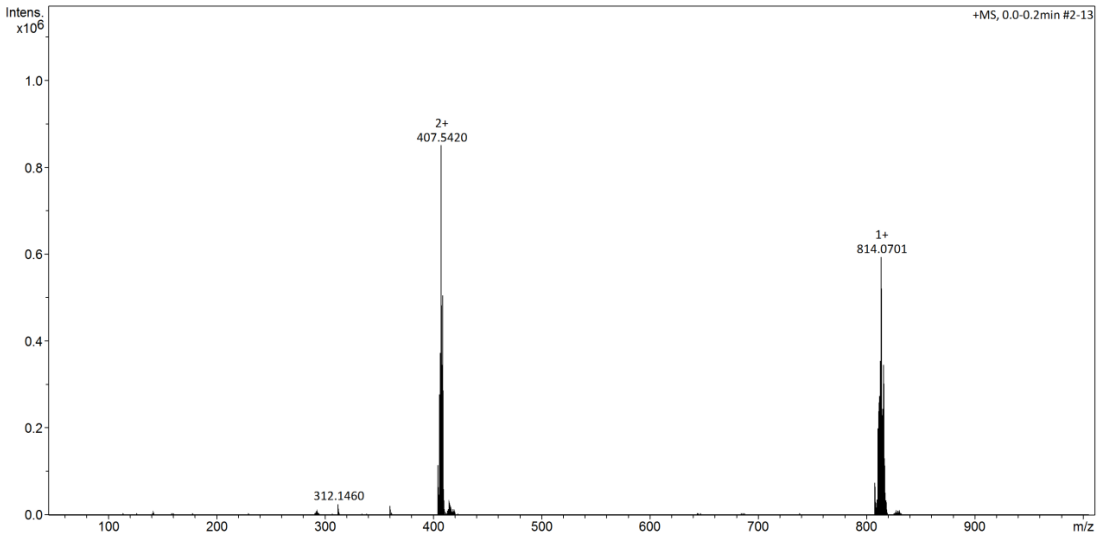


Figure S5. ESI-MS spectra of probe **Ru-LYP**

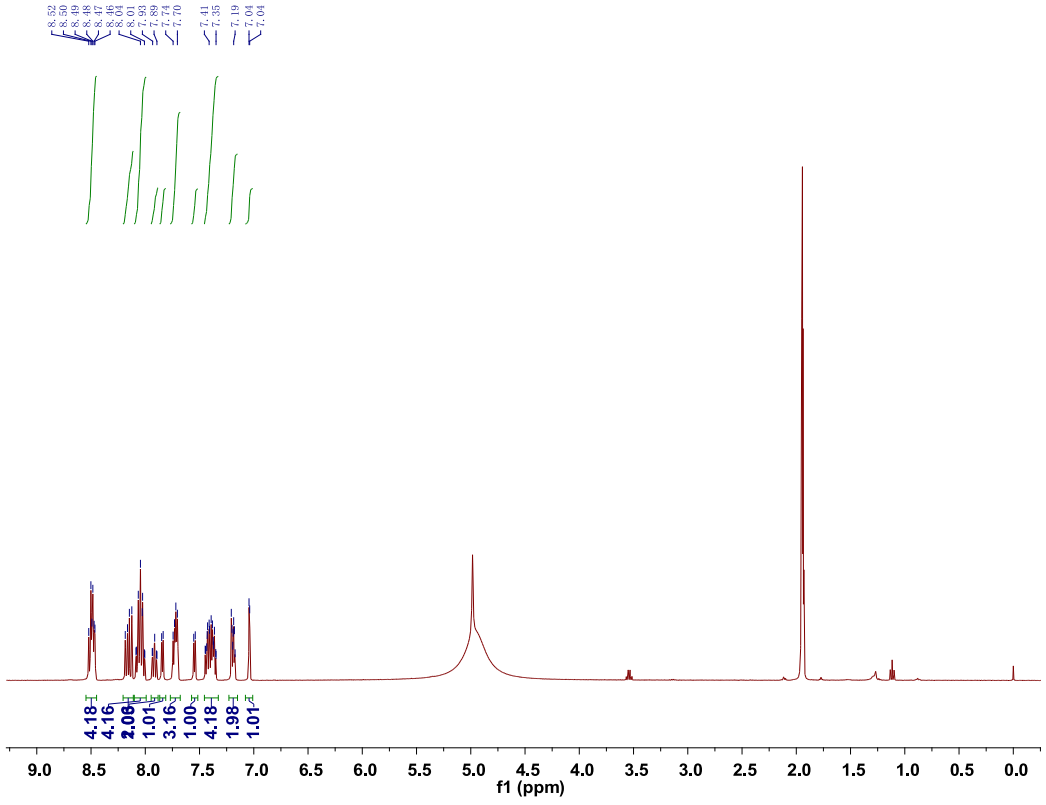


Figure S6. ^{1}H NMR spectrum of complex **Ru-NH$_2$** in CD_3CN

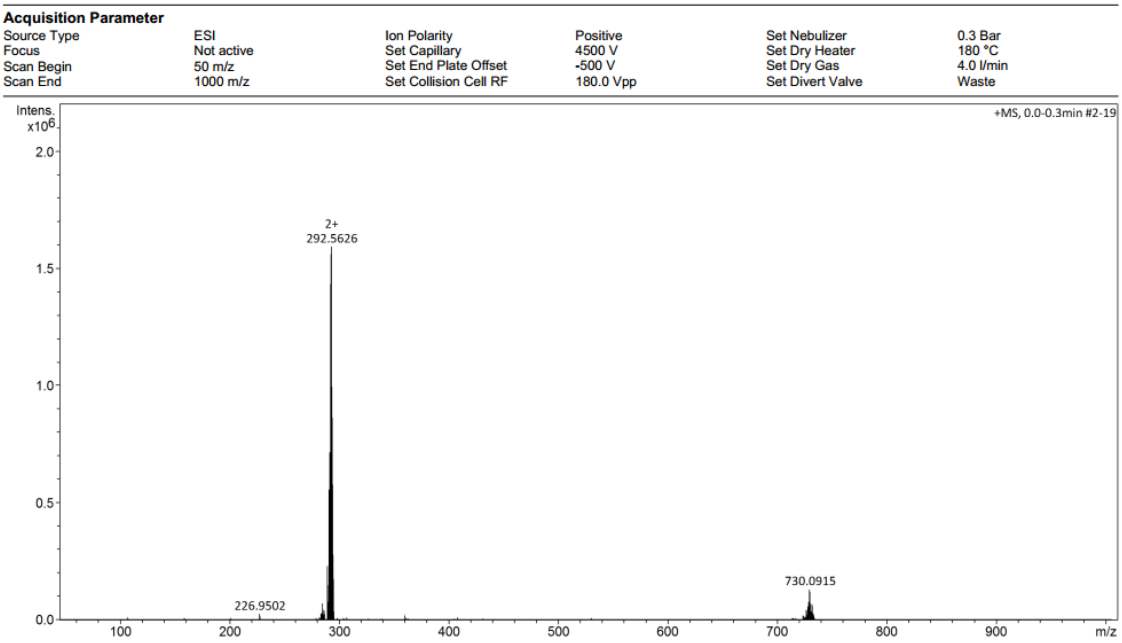


Figure S7. ESI-MS spectra of complex **Ru-NH$_2$**

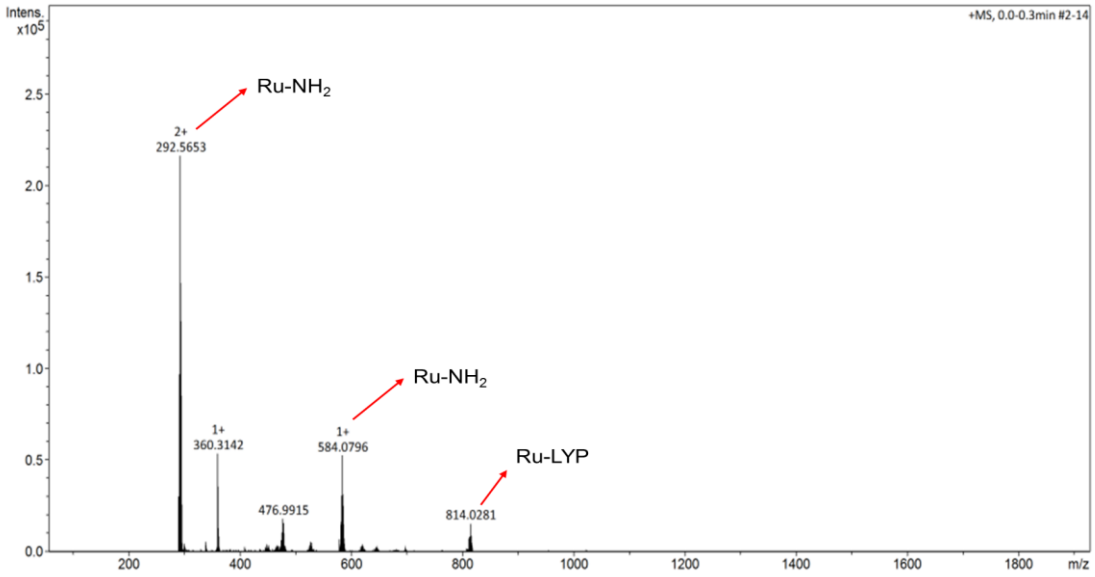


Figure S8. HRMS spectrum of the reaction product of Probe **Ru-LYP** with thiophenol (10 equiv)

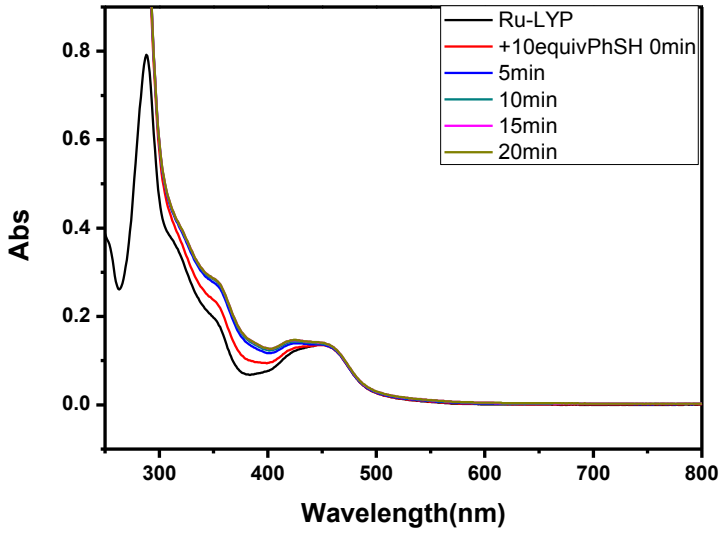


Figure S9. Absorption spectra of probe **Ru-LYP** (10.0 μM) in the presence of thiophenol (10.0 equiv.) in different reaction time in PBS buffer solution (0.01 M, pH = 7.4).

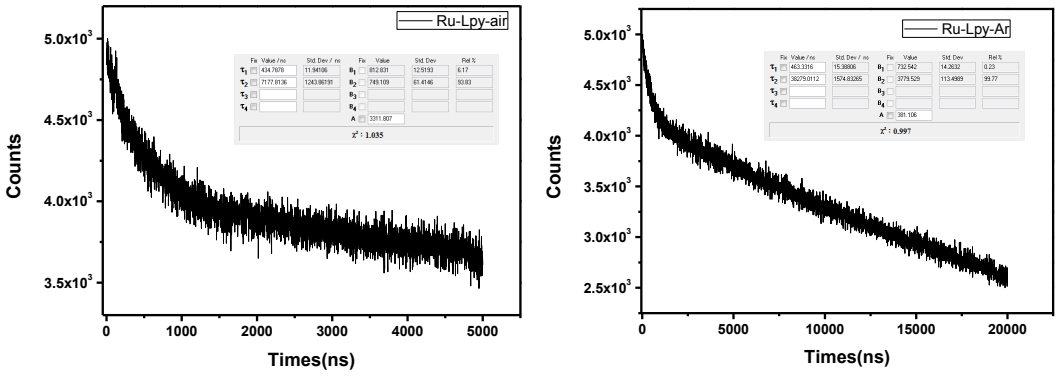


Figure S10. Phosphorescence decay curves of **Ru-LYP** (100 μM) in PBS solution (0.01 M, pH = 7.4) under air and Ar de-aerated condition.

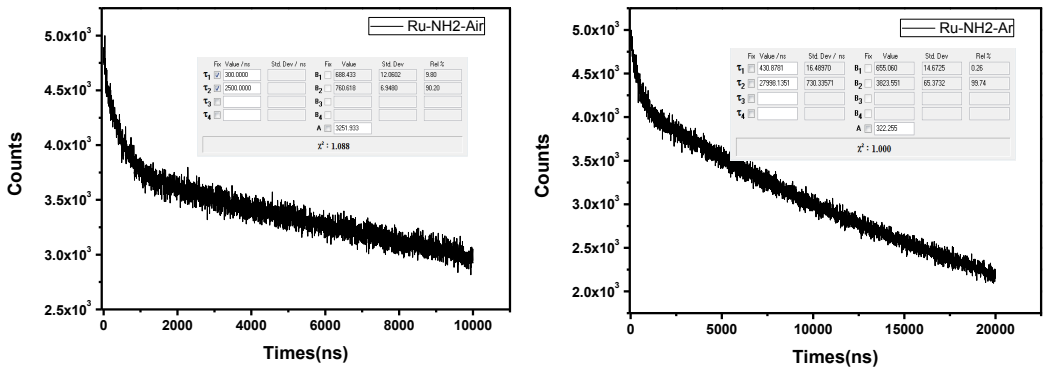


Figure S11. Phosphorescence decay curves of **Ru-NH$_2$** (100 μM) in PBS solution (0.01 M, pH = 7.4) under air and Ar de-aerated condition.

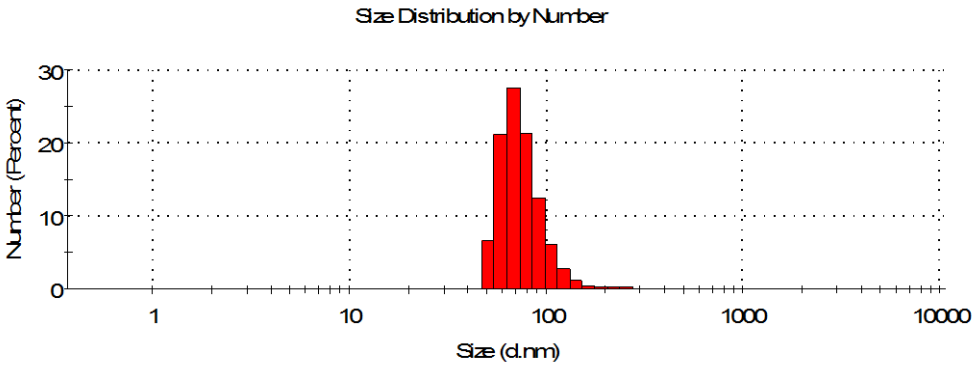


Figure S12. The dynamic light scattering data of complex **Ru-NH$_2$** nano aggregates in water.

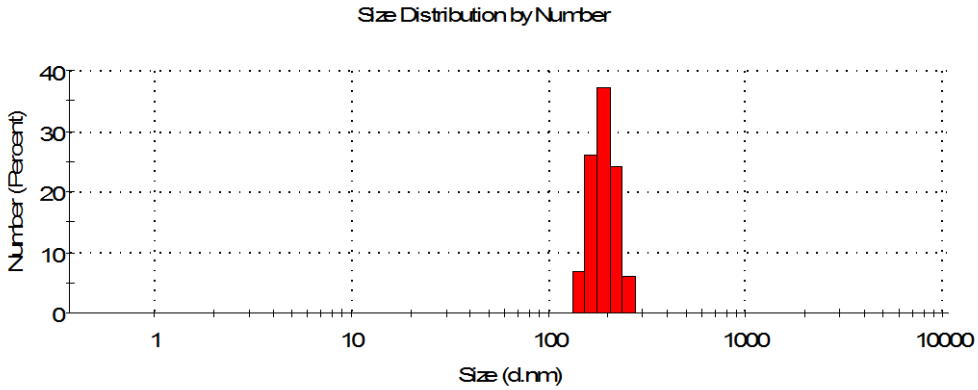


Figure S13. The dynamic light scattering data of probe **Ru-LYP** nano aggregates in water.

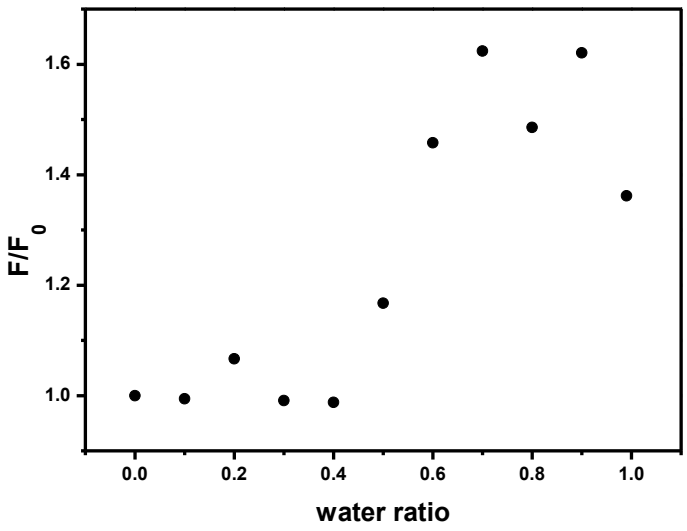


Figure S14. Emission intensity of the probe **Ru-LYP** (10 μM) in CH_3CN/H_2O mixtures with different water fractions (λex = 424 nm).

Table S1. The DFT data of probe **Ru-LYP** and compound **Ru-NH$_2$**

Ru-LYP

	x	y	z
Ru	-2.21699600	0.08671500	-0.05659600
C	-3.82733100	-2.13319100	-1.48805000

C	-2.86342700	-2.74140500	0.54984000
C	-4.36560600	-3.40197400	-1.67110700
H	-3.98280100	-1.34796600	-2.21809100
C	-3.37742500	-4.03623000	0.42035700
C	-4.13531200	-4.37357000	-0.69726200
H	-4.95005400	-3.61613100	-2.55938100
H	-3.18778400	-4.78013200	1.18462300
H	-4.53724400	-5.37595500	-0.80410500
C	-2.26227400	2.72647000	1.28806100
C	-0.17195900	2.37316700	0.30736400
C	-1.85211500	3.98295200	1.74444400
C	0.29737100	3.60619500	0.74938000
H	0.47510800	1.70707200	-0.24950000
C	-0.56165500	4.43125300	1.47328800
H	-2.52920300	4.60708200	2.31512600
H	1.32209800	3.88694800	0.53421200
H	-0.23412600	5.40254700	1.82993900
C	0.45895700	-1.17131800	-0.87063600
C	-0.70358600	-0.09598900	-2.59278200
C	1.53208300	-1.48547800	-1.71765900
H	0.48158800	-1.45496400	0.16992600
C	0.29784200	-0.45161400	-3.50217400
C	1.42317000	-1.13930900	-3.06992600
H	0.21951800	-0.17015700	-4.54540100
H	2.21769900	-1.38178600	-3.76928700
C	-3.84522100	1.69926300	-2.13588700
C	-1.88886100	0.70638500	-2.93606800
C	-4.14569900	2.23368000	-3.38346500
H	-4.49442300	1.86453200	-1.28446100
C	-2.13923000	1.21560800	-4.21544200
C	-3.27581700	1.98445400	-4.44556500
H	-5.04196700	2.83071500	-3.51223000
H	-1.44999400	1.01810400	-5.02778100
H	-3.47611100	2.38354700	-5.43468700
C	-2.05269000	-2.29434400	1.69947400
C	-0.86455400	-0.52514600	2.65199000
C	-1.72790100	-3.11472900	2.78430500
C	-0.50628600	-1.29334100	3.75428400
H	-0.53736800	0.50264400	2.55514900
C	-0.94814400	-2.61349300	3.82310400
H	-2.07785600	-4.13918800	2.82177200
H	0.10850700	-0.85913200	4.53495100
H	-0.68948700	-3.24466900	4.66706900
C	-4.99086600	0.30087900	1.28086300
C	-3.59138000	2.14851500	1.56665000
C	-6.01142700	0.89519100	2.01415200

H	-5.10981400	-0.68700900	0.85228300
C	-4.58183800	2.79849400	2.31107400
C	-5.80317800	2.17085100	2.53860000
H	-6.94478300	0.36419200	2.16685000
H	-4.40314100	3.78787200	2.71441500
H	-6.57557700	2.66880900	3.11580200
N	-2.74985200	0.94760800	-1.90396100
N	-1.42121300	1.93386900	0.56116400
N	-3.80639800	0.90324300	1.05130200
N	-3.09412000	-1.79644300	-0.40762800
N	-1.61891700	-1.00166900	1.64206300
N	-0.61017600	-0.47810200	-1.28685700
N	2.65836000	-2.16791400	-1.24260200
H	3.19127500	-2.72705600	-1.90195300
S	3.43309900	-2.01933000	0.25944300
O	3.99276400	-3.34142400	0.49599100
O	2.49637800	-1.38324800	1.18120700
C	4.87442600	-0.91620100	0.06637100
C	6.11542200	-1.55797300	0.06265000
C	4.84504300	0.49226600	0.11225700
C	7.30329500	-0.82153000	0.07410900
H	6.15024200	-2.64093000	0.08381400
C	6.01563800	1.23867800	0.16515000
C	7.23000500	0.56293400	0.13153800
H	8.27033100	-1.31054000	0.06079200
H	5.98899900	2.31994900	0.21666600
N	3.59762800	1.26286600	0.05522700
O	3.53927700	2.31214900	0.68315300
O	2.70073300	0.81965300	-0.66691300
N	8.48222100	1.35958500	0.16349100
O	8.35744900	2.57805500	0.20860800
O	9.53278500	0.73253400	0.14014300

Ru-NH_2

	x	y	z
Ru	-0.12344200	0.00217600	0.07538900
C	1.39040800	0.92277600	2.60286000
C	1.07246000	2.56049100	0.96938800
C	2.07867600	1.80679200	3.42689200
H	1.22156500	-0.10543600	2.89921600
C	1.75845900	3.49448100	1.75272200
C	2.26664300	3.11894700	2.99335000
H	2.45689100	1.46620400	4.38470800
H	1.90008300	4.50872900	1.39928000
H	2.79960400	3.83779800	3.60729200

C	-2.64336100	-0.99614600	-1.12097600
C	-0.81375100	-1.89178800	-2.26245200
C	-3.52250600	-1.70818300	-1.94366800
C	-1.63737900	-2.62227800	-3.11205800
H	0.26520100	-1.93401600	-2.35187500
C	-3.01940000	-2.52947500	-2.94889900
H	-4.59349900	-1.62816200	-1.80174800
H	-1.19794400	-3.24968200	-3.87999100
H	-3.69486500	-3.08633500	-3.59028100
C	2.53863900	-0.13102500	-1.47145800
C	2.15263000	-1.88087800	0.03446900
C	3.79719500	-0.64393700	-1.85812800
H	2.16022800	0.78366800	-1.91467800
C	3.39445900	-2.44241400	-0.30108500
C	4.21508500	-1.84012300	-1.23460300
H	3.72488200	-3.35895400	0.17311500
H	5.17365900	-2.28256300	-1.48870200
C	-0.83816700	-2.22890500	2.09438600
C	1.21939700	-2.46218300	1.00716800
C	-0.65857300	-3.40871200	2.80488900
H	-1.73172700	-1.62928800	2.22111800
C	1.45524700	-3.66015100	1.69525900
C	0.51398400	-4.13849200	2.59974300
H	-1.42185600	-3.74287800	3.49902100
H	2.36765600	-4.21871700	1.52407100
H	0.69209500	-5.06589900	3.13466300
C	0.49899900	2.86633300	-0.35592000
C	-0.63298700	2.01570000	-2.21247100
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H	-1.08674000	1.14870200	-2.67791900
C	-0.02706800	4.33407600	-2.20115500
H	0.99970200	4.96640100	-0.42578900
H	-1.07689700	3.35709800	-3.82854400
H	-0.00391400	5.31595900	-2.66285400
C	-2.40291600	1.31234900	1.69731300
C	-3.08273600	-0.10039000	-0.03306800
C	-3.71753000	1.60623400	2.04238600
H	-1.57046000	1.74626400	2.23841900
C	-4.42471200	0.15753200	0.26599800
C	-4.74931100	1.01692000	1.31200000
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H	-5.78808800	1.22191700	1.54999200
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N	-1.29229800	-1.09260800	-1.28775100

N	-2.07908000	0.47894800	0.68806600
N	0.89114000	1.27880000	1.40217500
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N	1.74925500	-0.72456400	-0.56519900
N	4.55144800	-0.01961600	-2.79854600
H	4.28593800	0.87538600	-3.18113800
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