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Supporting Information

A novel turn-on fluorogenic aldehyde-appended salamo-like copper(II) complex probe for simultaneous detection of $S_2O_3^{2-}$ and GSH

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2. Experimental Section

2.1 Materials and Physical Measurements.

Unless specifically stated, all the chemicals in this paper were obtained from commercial sources and used directly without any further purification. For sensing studies of anions, all the anions were used in the form of sodium or potassium salts. A German Bruker AVANCE DRX-400 spectrometer was used to record the 1H , and ^{13}C NMR spectra in $CDCl_3$ solution and chemical shifts were recorded in ppm, where tetramethylsilane (TMS) was used as an internal standard. Electrospray ionization mass spectra (ESI-MS) were collected on the Bruker Daltonics Esquire 6000 mass spectrometer. IR spectra were recorded in the range of 4000-400 cm^{-1} using a Vertex70 FT-IR spectrophotometer via KBr pelletization technique. All pH values were measured by using a pH-10C digital pH meter. The electrochemical data were recorded with a CHI660E electrochemical workstation and 0.1 M tetrabutylammonium perchlorate (TBAP) dichloromethane solution was used as the supporting electrolyte. The working electrode was a glassy carbon electrode (GCE). The reference electrode was saturated calomel electrode (SCE), with graphite as counter electrode. Fluorescence and UV-vis measurements were done using a

Perkin-Elmer LS-55 spectrophotometer and Shimadzu UV-2550 spectrophotometer at room temperature, respectively.

2.2 Crystallographic data collection and refinement.

The single-crystal X-ray diffraction collection was taken on a Bruker Smart 1000 CCD area detector. Suitable crystal data of the copper(II) complex was obtained at 173 K on a Bruker Smart 1000 CCD area detector using Mo-K α radiation ($\lambda = 0.71073$ Å). Data collection and reduction were performed using the SMART and SAINT software.¹ The crystal structure was determined by direct methods, and the subsequent refinement operation was agented by full-matrix least-squares on F^2 using the SHELXTL-97² and Olex2 program.³ Moreover, all H atoms were placed geometrically, and all non-H atoms were refined anisotropically.

2.3 Synthesis and characterization of compounds.

The synthesis procedure of complex crystal $[\text{Cu}_4(\text{L})_2(\text{MeOH})_2(\text{H}_2\text{O})_2] \text{MeOH}$, probe **ASC**, **ASC-S₂O₃²⁻** adduct and **ASC-GSH** adduct was carried out. The details of experiments were described as follows.

Preparation of H₄L. The 2-[*O*-(1-ethoxyamide)]oxime-6-methoxyphenol and 2,3-dihydroxynaphthalene-1,4-dicarbaldehyde were prepared via the modified procedure of the reported method in the literature.⁴ The aldehyde-appended salamo-like ligand (**H₄L**) was synthesized based on the two precursors mentioned above. ¹H NMR spectrum of the ligand **H₄L** is shown in **Fig. S1** and ESI-MS spectrum is displayed in **Fig. S2**.

¹H NMR (400 MHz, CDCl₃), δ (ppm): 13.24 (s, 1H, -OH), 10.99 (s, 1H, -OH), 10.84 (s, 1H, -CHO), 9.92 (s, 1H, -OH), 9.12 (s, 1H, -C=N), 8.35-8.36 (dd, 1H, NaH), 8.25 (s, 1H, -C=N), 7.96-7.97 (dd, 1H, NaH), 7.47-7.54 (m, 2H, NaH), 6.93-6.95 (dd, 1H, ArH), 6.80-6.83 (t, $J = 4$ Hz, 1H, ArH), 6.74-6.76 (dd, 1H, ArH), 5.53 (s, 1H, -OH), 4.55-4.63 (m, 4H, -CH₂). ESI-MS calculated for C₂₁H₁₈N₂O₇: 410.11 (M), found: 409.10 (M-H). IR (KBr pellet, cm⁻¹): 3429 (ν O-H), 1743 (ν C=O), 1611 (ν C=N), 1175 (ν Ar-O) (**Fig. S12**). UV-Vis (DMF : H₂O, 20 μ M), λ_{abs} ($\epsilon \times 10^4$ dm³

mol⁻¹ cm⁻¹): 345 nm (2.04) and 406 nm (1.52).

Preparation of complex crystal [Cu₄(L)₂(MeOH)₂(H₂O)₂] MeOH. A methanol solution (3 mL) of Cu(ClO₄)₂ 6H₂O (3.70 mg, 0.01 mmol) was added drop-wise into a dichloromethane and chloroform (3:1 v/v) mixed solution (4 mL) containing H₄L (2.05 mg, 0.005 mmol), followed by drop-wise addition of diluted NEt₃ (1.00 mg, 0.01 mmol). The dark brown reaction mixture was stirred at ambient temperature for 0.5 h. Finally the black block-shaped crystals of the copper(II) complex, suitable for X-ray diffraction, were formed after four weeks on slow evaporation of the filtrate in air. [Cu₄(L)₂(MeOH)₂(H₂O)₂] MeOH, yield: 7.24 mg (62.9%).

Preparation of probe ASC. H₄L (8.2 mg, 0.02 mmol) was dissolved in 2 mL CH₂Cl₂ and 1.5 mL methanol solution containing Cu(ClO₄)₂ 6H₂O (14.8 mg, 0.04 mmol) was added to the reaction mixture. The reaction mixture was stirred at RT for 0.5 h. The precipitate formed was filtered and washed with cold MeOH to give **ASC** as a black solid (7.86 mg, 73.8%). ESI-MS calculated for C₂₁H₁₄N₂O₇Cu₂: 531.94 (M), found: 532.95 (M+H). IR (KBr pellet, cm⁻¹): 1729 (νC=O), 1600 (νC=N), 1163 (νAr-O), 549 (νCu-N), 483 (νCu-O) (**Fig. S12**). UV-Vis (DMF : H₂O, 20 μM), λ_{abs} (ε × 10⁴ dm³ mol⁻¹ cm⁻¹): 382 nm (2.05).

Preparation of ASC-S₂O₃²⁻ and ASC-GSH adduct. Cu(ClO₄)₂ 6H₂O (7.4 mg, 0.02 mmol) in MeOH (1 mL) was added to a CH₂Cl₂ solution (2 mL) of the ligand **H₄L** (4.1 mg, 0.01 mmol). The mixture was stirred for 30 min at room temperature. A methanolic solution (0.5 mL) containing Na₂S₂O₃ 5H₂O (15.0 mg, 0.06 mmol) and a little drops of water was added into it thereafter and stirring was continued for 1 hour. The light yellow colored mass (**ASC-S₂O₃²⁻**) was obtained by filtration followed by washing with cold MeOH and then dried in vacuo for performing the characterization. The synthesis of **ASC-GSH** adduct is similar to that of **ASC-S₂O₃²⁻**, except the final methanolic solution containing GSH (12.5 mg, 0.04 mmol) and a little drops of water. **ASC-S₂O₃²⁻**. ESI-MS calculated for C₂₁H₁₈N₂O₇: 410.11 (M), found: 433.10 (M+Na). IR (KBr pellet, cm⁻¹): 1733 (νC=O), 1610 (νC=N), 1174 (νAr-O) (**Fig. S12**). UV-Vis (DMF : H₂O, 20 μM), λ_{abs} (ε × 10⁴ dm³ mol⁻¹ cm⁻¹): 363 nm (2.09). **ASC-GSH.**

ESI-MS calculated for $C_{21}H_{18}N_2O_7$: 410.11 (M), found: 411.15 (M+H). IR (KBr pellet, cm^{-1}): 1742 ($\nu C=O$), 1610 ($\nu C=N$), 1175 ($\nu Ar-O$) (**Fig. S12**). UV-Vis (DMF : H_2O , 20 μM), λ_{abs} ($\epsilon \times 10^4 dm^3 mol^{-1} cm^{-1}$): 346 nm (2.01) and 405 nm (1.53).

2.4 Analysis procedure.

A stock solution of probe **ASC** (1.0 mM) was prepared in 10 mL of DMF. Anions stock solutions of the potassium or sodium salts of $S_2O_3^{2-}$, NO_2^- , SiO_3^{2-} , CO_3^{2-} , CrO_4^{2-} , $S_2O_8^{2-}$, $B_4O_7^{2-}$, F^- , WO_4^{2-} , CN^- , HS^- , $H_2PO_4^-$, HSO_4^- , SO_3^{2-} , S^{2-} and SCN^- were prepared at 10 mM in 10 mL aqueous DMF solution respectively. Stock solutions (10 mM) of the various amino acids and peptide such as glutathione (GSH), Glu, Phe, Gly, Arg, Pro, Ser, Thr, Val, Ile, Met, Cys, Lys, Asn, Asp and Leu were separately dissolved in 10 mL aqueous DMF solution.

For the fluorescence experiment of probe **ASC** detecting $S_2O_3^{2-}$, the test solutions were prepared by placing 10 μL of the probe stock solution into a colorimetric dish with adding 10 μL each anionic stock solution, and diluting these stock solutions to 2 mL with DMF solution with 10% water. Also, in the fluorescence experiment of probe **ASC** detecting GSH, the test solutions were prepared by placing 20 μL of the probe stock solution into a colorimetric dish with adding 20 μL each anionic stock solution, and diluting these stock solutions to 2 mL with DMF solution with 10% water.

For UV-Visible absorbance spectral measurements, probe **ASC** was further diluted to 2 mL with DMF : water (9:1, v/v) to give desired concentration 20 μM and then absorption spectra were recorded by adding 40 μL of each anions and amino acids to the solution of **ASC** at room temperature.

Determination of K_a of **H₄L** detecting Cu^{2+} .

The binding constant was calculated from the UV titration curve according to Benesi-Hildebrand equation as shown below:

$$\log (A-A_{min})/(A_{max}-A) = \log K_a + 2 \log [Cu^{2+}]$$

$$K_a = 6.09 \times 10^9 M^{-1}$$

Determination of LOD, LOQ and K_a of ASC detecting $S_2O_3^{2-}$.

The fluorescence detection limit and quantification limit of **ASC** toward $S_2O_3^{2-}$ was examined from the titration experiment of probe **ASC** with $S_2O_3^{2-}$. The below equations were used for determining the LOD, LOQ and K_a .

$$\text{Linear Equation: } y = 60.363 \times x + 4.2308 \quad R^2 = 98925$$

$$S = 6.0363 \times 10^7 \quad \delta = \sqrt{\frac{\sum (F_0 - \bar{F}_0)^2}{N - 1}} = 3.0175 \quad (N=20) \quad K=3$$

$$\text{LOD} = K \times \delta / S = 1.4997 \times 10^{-7} \text{ M}$$

$$\text{LOQ} = 10 \times \delta / S = 4.9989 \times 10^{-7} \text{ M}$$

Where N , S , F_0 and \bar{F} are the number of replicates for the measurements, slope, fluorescence intensity and mean of fluorescence intensity of the blank solution of probe **ASC**, respectively.

The binding constant was calculated from the fluorescence titration curve according to Benesi-Hildebrand equation as shown below:

$$\log (F - F_{\min}) / (F_{\max} - F) = \log K_a + 2 \log [S_2O_3^{2-}]$$
$$K_a = 5.74 \times 10^9 \text{ M}^{-1}$$

Determination of LOD, LOQ and K_a of ASC detecting GSH.

The fluorescence detection limit and quantification limit of **ASC** toward GSH was examined from the titration experiment of probe **ASC** with GSH. The below equations were used for determining the LOD, LOQ and K_a .

$$\text{Linear Equation: } y = 68.726 \times x - 321.87 \quad R^2=0.96705$$

$$S = 6.8726 \times 10^7 \quad \delta = \sqrt{\frac{\sum (F_0 - \bar{F}_0)^2}{N - 1}} = 3.0175 \quad (N=20) \quad K=3$$

$$\text{LOD} = K \times \delta / S = 1.3172 \times 10^{-7} \text{ M}$$

$$\text{LOQ} = 10 \times \delta / S = 4.3906 \times 10^{-7} \text{ M}$$

Where N , S , F_0 and \bar{F} are the number of replicates for the measurements, slope, fluorescence intensity and mean of fluorescence intensity of the blank solution of probe **ASC**, respectively.

The binding constant was calculated from the fluorescence titration curve according to Benesi-Hildebrand equation as shown below:

$$\log (F - F_{\min}) / (F_{\max} - F) = \log K_a + 2 \log [\text{GSH}]$$
$$K_a = 1.11 \times 10^9 \text{ M}^{-1}$$

Table S1. Detailed crystal and structure refinement data of the copper(II) complex.

Complex CCDC	[Cu ₄ (L) ₂ (MeOH) ₂ (H ₂ O) ₂] MeOH 2071007
Empirical formula	C ₄₅ H ₄₄ Cu ₄ N ₄ O ₁₉
Formula weight	1199.00
Temperature (K)	173.0
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	P42/n
a (Å)	19.1223(3)
b (Å)	19.1223(3)
c (Å)	12.5887(3)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	4603.21(18)
Z	4
D _c (Mg /m ³)	1.730
μ (mm ⁻¹)	1.908
F(000)	2440.0
Crystal size (mm)	0.19 × 0.17 × 0.16
θ Range (°)	2.21 to 26.753 -23 ≤ h ≤ 24
Index ranges	-24 ≤ k ≤ 24 -15 ≤ l ≤ 15
Reflections collected / unique	57931 / 4881
R _{int}	0.0418
Completeness to θ = 25.00	99.8 %
Data/restraints/parameters	4881 / 16 / 341
Final R indices [I > 2σ(I)]	R1 = 0.0429 wR2 = 0.1341
R indices (all data)	R1 = 0.0513 wR2 = 0.1419
Δρ _{max,min} (e Å ⁻³)	1.08 and -0.77

Table S2. Selected bond distances (Å) and bond angles (°) for the copper(II) complex.

Bond	Bond distance (Å)	Bond	Bond distance (Å)	Bond	Bond distance (Å)
Cu1–O1	1.988(2)	Cu2–O2 [#]	1.958(2)	Cu3–O6	1.985(2)
Cu1–O6	1.956(2)	Cu2–O2	1.958(2)	Cu3–O7	1.869(3)
Cu1–O8	2.357(2)	Cu2–O1	1.891(3)		
Cu1–N1	1.969(3)	Cu2–O1 [#]	1.891(3)		
Cu1–N2	2.003(3)	Cu3–O6 [#]	1.985(2)		
Bond	Bond angle (°)	Bond	Bond angle (°)	Bond	Bond angle (°)
O2–Cu1–O8	96.90(10)	N2–Cu1–O8	103.13(11)	O6–Cu3–O6 [#]	160.80(14)
O2–Cu1–N2	159.66(11)	N1–Cu1–N2	98.54(12)	O7–Cu3–O6 [#]	96.79(10)
O6–Cu1–O2	89.15(10)	O2 [#] –Cu2–O2	164.80(15)	O7 [#] –Cu3–O6	96.78(10)
O6–Cu1–O8	85.94(9)	O1 [#] –Cu2–O2	96.97(10)	O7–Cu3–O6	85.44(10)
O6–Cu1–N1	171.28(11)	O1 [#] –Cu2–O2 [#]	84.68(10)	O7 [#] –Cu3–O6 [#]	85.44(10)
O6–Cu1–N2	88.77(11)	O1–Cu2–O2 [#]	96.98(10)	O7–Cu3–O7 [#]	166.71(19)
N1–Cu1–O2	85.62(11)	O1–Cu2–O2	84.68(10)		
N1–Cu1–O8	87.76(11)	O1 [#] –Cu2–O1	167.54(16)		

Symmetry code (#): -x+3/2, -y+1/2, z

Table S3. Intramolecular and intermolecular interactions of note in the copper(II) complex.

Donor (D) \cdots Acceptor (A)	D–H (Å)	H \cdots A (Å)	D \cdots A (Å)	D–H \cdots A (deg.)	Symmetry Element
Hydrogen bond					
O8–H8 \cdots O7 [#]	0.88	1.85	2.64	148	3/2-x,1/2-y,z
O9–H9B \cdots O1 [#]	0.87	2.07	2.69	128	3/2-x,1/2-y,z
O9–H9A \cdots O2	0.87	2.34	2.91	123	
O10–H10 \cdots O9	0.84	2.25	2.84	127	
O9 [#] –H9A [#] \cdots O2 [#]	0.87	2.34	2.91	123	
O8 [#] –H8 [#] \cdots O7	0.88	1.85	2.64	148	3/2-x,1/2-y,z
O9 [#] –H9B [#] \cdots O1	0.87	2.07	2.69	128	3/2-x,1/2-y,z
C5–H5 \cdots O3	0.95	2.77	3.57	143	
C12–H12 \cdots O3	0.95	3.23	3.63	107	
C22–H22C \cdots O3	0.98	2.50	3.37	148	1+y,3/2-x,3/2-z

Cartesian coordinates, used charge and multiplicity for all optimized structures of the stationary points.

ASC

Charge = 0 Multiplicity = 1

Cu	-1.29222	1.275	-0.25048
Cu	-0.51762	-1.65677	-0.70368
O	0.2602	-0.0929	-0.91577
O	-1.93392	-0.66681	-0.55693
O	1.14912	-2.34723	-0.61615
O	-1.52146	-3.04729	-0.21332
O	-0.29458	3.60392	0.64048
O	-3.34722	2.97698	0.13671
O	4.99819	-3.31323	0.21928
N	0.18168	2.40548	-0.02823
N	-3.12771	1.54516	0.11309
C	-2.96938	-1.27201	0.06589
C	-4.07363	-0.60331	0.53254
C	4.1923	-0.37431	0.1835
C	1.53284	-0.06914	-0.50906
C	2.08126	-1.38431	-0.41822
C	3.59889	0.91135	0.20196
C	-5.08223	-1.3783	1.12385
H	-5.96792	-0.90412	1.49722
C	-4.13358	0.86287	0.46996
H	-5.04326	1.35242	0.76374
C	1.43326	2.26529	0.1695
H	1.94082	3.05878	0.67935
C	2.18709	1.04203	-0.11189
C	5.56817	-0.48392	0.47718
H	6.00499	-1.45554	0.47102
C	4.40292	2.02859	0.50025
H	3.97717	3.0101	0.49318

C	3.38563	-1.54979	-0.09825
C	-2.76601	-2.63533	0.22455
C	6.31987	0.61936	0.76657
H	7.36385	0.51164	0.98356
C	5.73346	1.88928	0.77633
H	6.32756	2.754	0.99421
C	-4.9237	-2.74254	1.23787
H	-5.69819	-3.32722	1.69094
C	-2.40011	3.58799	-0.79943
H	-2.9703	4.28241	-1.39411
H	-2.01291	2.80592	-1.42031
C	3.86599	-2.93509	-0.03238
H	3.08767	-3.65504	-0.24058
C	-1.26003	4.36636	-0.15031
H	-0.72895	4.87602	-0.94275
H	-1.64252	5.08881	0.55172
C	-3.75588	-3.3862	0.80072
H	-3.63585	-4.4421	0.92812

L⁴⁻

Charge = -4 Multiplicity = 1

C	-4.76421	3.67656	-0.72911
C	-5.64302	2.66697	-0.39027
C	-5.2308	1.34365	-0.17901
C	-3.84342	1.05534	-0.27409
C	-2.97247	2.10808	-0.59181
C	-3.41496	3.39288	-0.83364
H	-5.12954	4.67322	-0.88669
H	-6.67314	2.9291	-0.27066
C	-6.17195	0.2784	0.17672
C	-3.3685	-0.30219	-0.00274
H	-1.91804	1.93327	-0.63569
H	-2.70922	4.16377	-1.07738
C	-4.21955	-1.29468	0.50416

C	-5.71381	-0.98514	0.61546
C	-1.99767	-0.62533	-0.2784
H	-1.43211	0.11667	-0.80975
C	0.75539	-2.7302	-0.24515
H	0.28072	-3.60043	-0.68064
H	0.82185	-2.87076	0.82511
C	2.14971	-2.56143	-0.82543
H	2.08076	-2.25108	-1.8592
H	2.681	-3.50367	-0.78038
N	-1.36055	-1.70306	0.00068
O	0.0041	-1.5477	-0.55428
N	4.20526	-1.42228	-0.56033
O	2.83069	-1.5703	-0.04224
O	-3.86401	-2.44675	0.83825
O	-6.43148	-1.90924	1.043
C	-7.57059	0.49406	0.04032
H	-7.81618	1.42924	-0.46017
O	-8.52693	-0.2259	0.3624
C	4.79128	-0.51246	0.12163
H	4.26037	-0.01372	0.91065
C	6.1398	-0.06607	-0.06134
C	6.98388	-0.62547	-1.07296
C	6.56904	0.95174	0.81673
C	8.24724	-0.16808	-1.20511
H	6.58953	-1.39984	-1.70438
C	7.97604	1.45709	0.65251
C	8.72945	0.8629	-0.34696
H	8.90262	-0.57287	-1.95732
H	9.74017	1.21217	-0.47416
O	5.82305	1.44918	1.72449
O	8.39245	2.39231	1.43203

H₄L

Charge = 0 Multiplicity = 1

C	7.02824	3.08561	-0.00057
C	7.34885	1.74029	-0.00028
C	6.34529	0.73687	-0.00005
C	4.96208	1.13526	-0.0001
C	4.67496	2.52846	-0.00046
C	5.67702	3.48184	-0.00067
H	7.81618	3.83128	-0.00073
H	8.39446	1.45792	-0.00023
C	6.67619	-0.67358	0.00019
C	3.90565	0.12794	0.00015
H	3.65012	2.87332	-0.00062
H	5.4184	4.53534	-0.00095
C	4.26811	-1.21509	0.0003
C	5.63305	-1.60411	0.00034
C	2.5109	0.55065	0.00035
H	2.29013	1.61267	0.00095
C	-0.87368	-0.37743	0.00001
H	-0.85217	-1.01176	0.89035
H	-0.8521	-1.01111	-0.89079
C	-2.08874	0.5365	0.00028
H	-2.10691	1.17201	-0.89035
H	-2.10698	1.17139	0.89136
N	1.49957	-0.26553	-0.00008
O	0.27935	0.52153	0.00038
N	-4.46016	0.42348	0.00009
O	-3.2367	-0.3628	-0.00008
O	3.33565	-2.21927	0.00052
H	3.80349	-3.08528	0.00072
O	5.82771	-2.9573	0.00057
H	6.82078	-3.14389	0.00061
C	8.02852	-1.18197	0.00029
H	8.86349	-0.4754	0.00019
O	8.30672	-2.42074	0.00049
C	-5.48631	-0.36449	-0.00018

H	-5.36208	-1.44423	-0.00048
C	-6.84379	0.17725	-0.0001
C	-7.11169	1.56453	0.00026
C	-7.92925	-0.71254	-0.00039
C	-8.41969	2.03951	0.00032
H	-6.27178	2.24838	0.00049
C	-9.2451	-0.22377	-0.00033
C	-9.50179	1.14161	0.00003
H	-8.61113	3.10673	0.0006
H	-10.52456	1.50798	0.00007
O	-7.70628	-2.07854	-0.00075
H	-8.56591	-2.5492	-0.00093
O	-10.21959	-1.23087	-0.00065
H	-11.12708	-0.8778	-0.00063

Figure Legends:

Fig. S1. ^1H NMR spectrum of ligand **H₄L** in CDCl_3 .

Fig. S2. ESI mass spectra of **H₄L** in DMF.

Fig. S3. Visualization of the copper(II) complex intramolecular interactions by IGM.

Fig. S4. Crystal packing 2D network structure of the copper(II) complex assisted supramolecular cyclic hydrogen-bonded motif.

Fig. S5. Crystal packing 3D layered structure of the copper(II) complex in solid-state viewed along a-axis (**A**), b-axis (**B**) and c-axis (**C**).

Fig. S6. (**A**) Benesi-Hildebrand plot (at 386 nm) of **H₄L** (20 μM), assuming 1:2 stoichiometry for association between **H₄L** and Cu^{2+} . (**B**) Job plot of **H₄L** and Cu^{2+} , where the absorbance at 386 nm was plotted against the mole fraction of Cu^{2+} . The total concentration of Cu^{2+} with **H₄L** was 2.0×10^{-5} M.

Fig. S7. ESI-MS of **ASC** in aqueous DMF solution.

Fig. S8. Cyclic voltammetry curve of probe **ASC** at different scan rates [reference: saturated calomel electrode; supporting electrolyte: 0.1M TBAP dichloromethane solution; scan rate: = 50 mV s^{-1}].

Fig. S9. UV-absorption spectra of the aqueous DMF solution (2.0×10^{-5} M) of **H₄L**, **ASC**, **ASC** with $\text{S}_2\text{O}_3^{2-}$ recorded at 298 K and atmospheric pressure.

Fig. S10. Absorption spectra of the aqueous DMF solution (2.0×10^{-5} M) of **H₄L**, **ASC**, **ASC** with GSH recorded at 298 K and atmospheric pressure.

Fig. S11. Cyclic voltammogram of **H₄L**, **ASC**, **ASC+Na₂S₂O₃** adduct and **ASC+GSH** adduct at room temperature (inset: CV of **ASC**) [reference: saturated calomel electrode; supporting electrolyte: 0.1M TBAP dichloromethane solution; scan rate: = 50 mV s⁻¹].

Fig. S12. FT-IR data comparison of **H₄L** (A), **ASC** (B), **ASC-S₂O₃²⁻** (C) and **ASC-GSH** (D) in solid-state.

Fig. S13. ESI-MS of **ASC** adding thiosulfate ion in aqueous DMF solution.

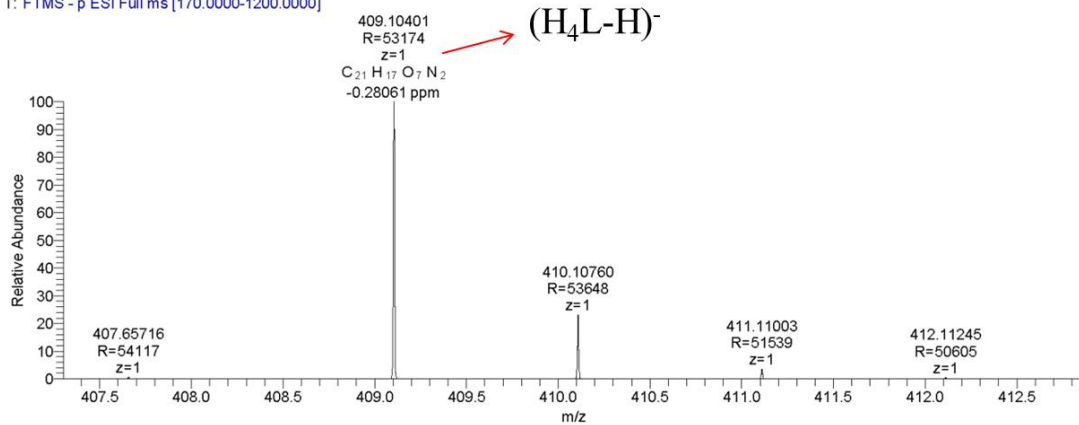
Fig. S14. ESI-MS of **ASC** adding glutathione in aqueous DMF solution.

Fig. S15. Electron cloud distributions and energy gap of the selected frontier orbitals of the copper(II) complex.

Fig. S16. Lowest-energy structures of **ASC** (A), **(L)⁴⁺** (B), and **H₄L** (C) in DMSO.

Fig. S17. Energy level diagram and frontier molecular orbitals for **ASC**, **(L)⁴⁺**, **H₄L** and contribution analysis of orbital transition in electron excitation.

DENGYUNHU-1 #31-59 RT: 0.13778-0.26258 AV: 29 NL: 2.70E7
T: FTMS - p ESI Full ms [170.0000-1200.0000]



DENGYUNHU-1 #31-59 RT: 0.13778-0.26258 AV: 29
T: FTMS - p ESI Full ms [170.0000-1200.0000]
m/z= 407.30160-412.86909

m/z	Intensity	Relative	Resolution	Charge	Delta (ppm)	Composition
407.65716	169997.3	0.62	54117.34	1.00		
409.10401	27322390.0	100.00	53173.61	1.00	-0.28	C ₂₁ H ₁₇ O ₇ N ₂
410.10760	6262644.0	22.92	53648.25	1.00		
411.11003	958791.2	3.51	51538.88	1.00		
412.11245	110921.4	0.41	50605.46	1.00		

Fig. S2.

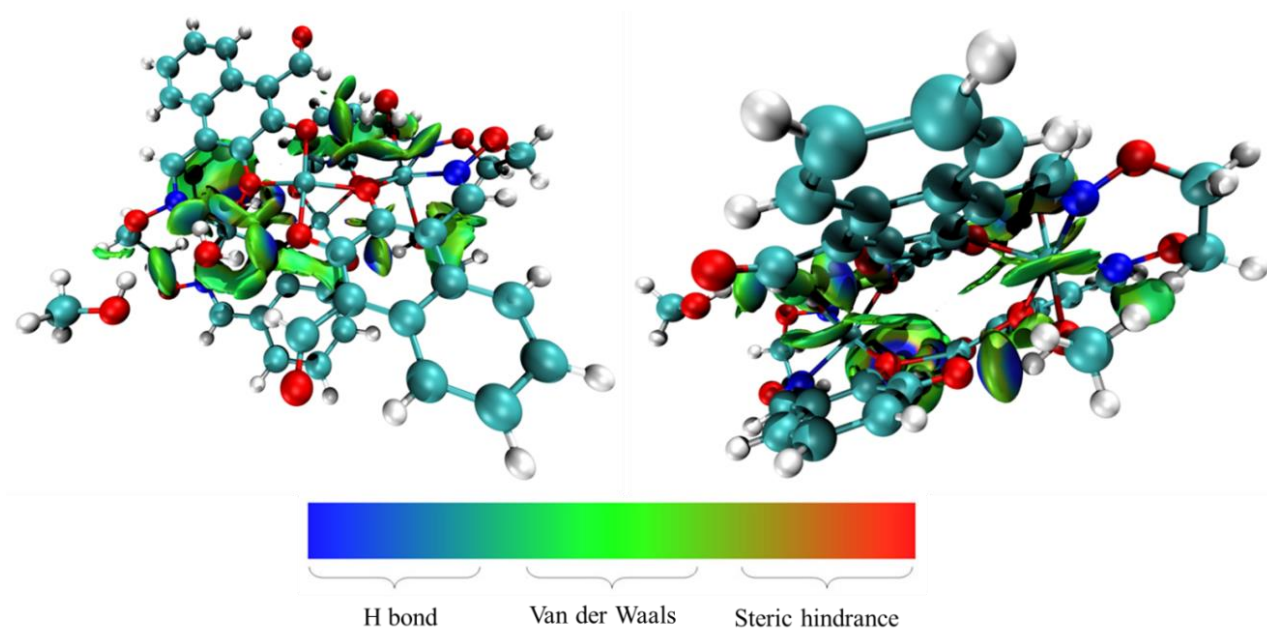


Fig. S3.

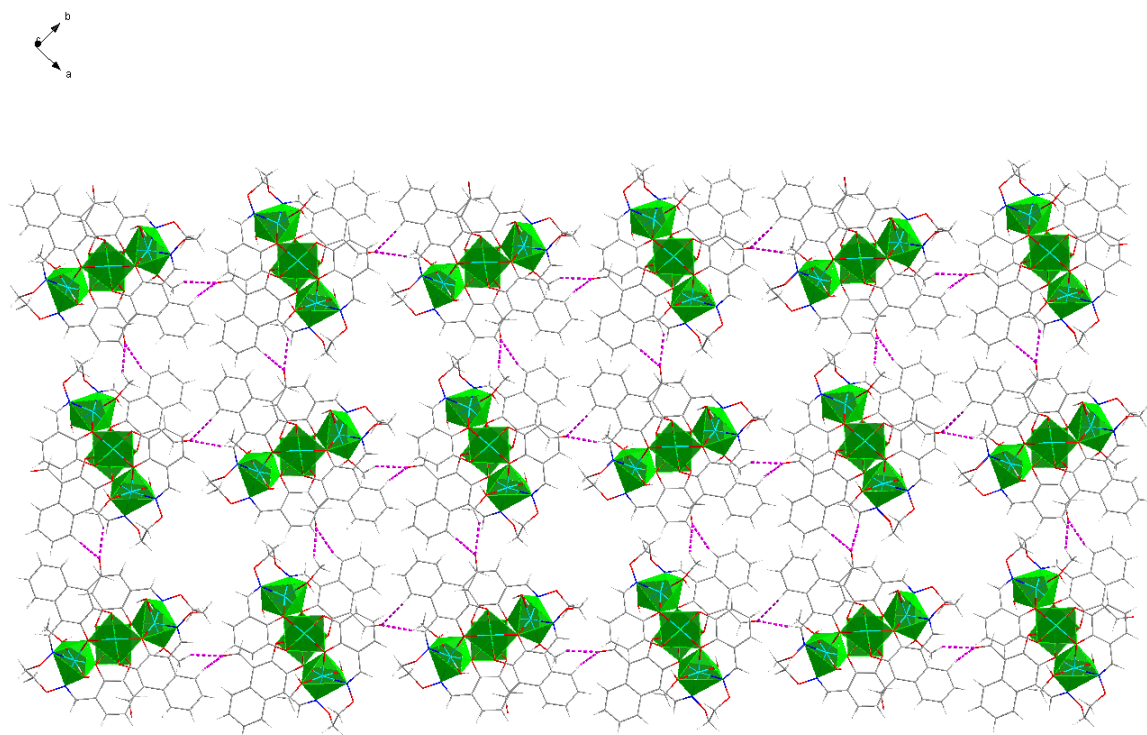


Fig. S4.

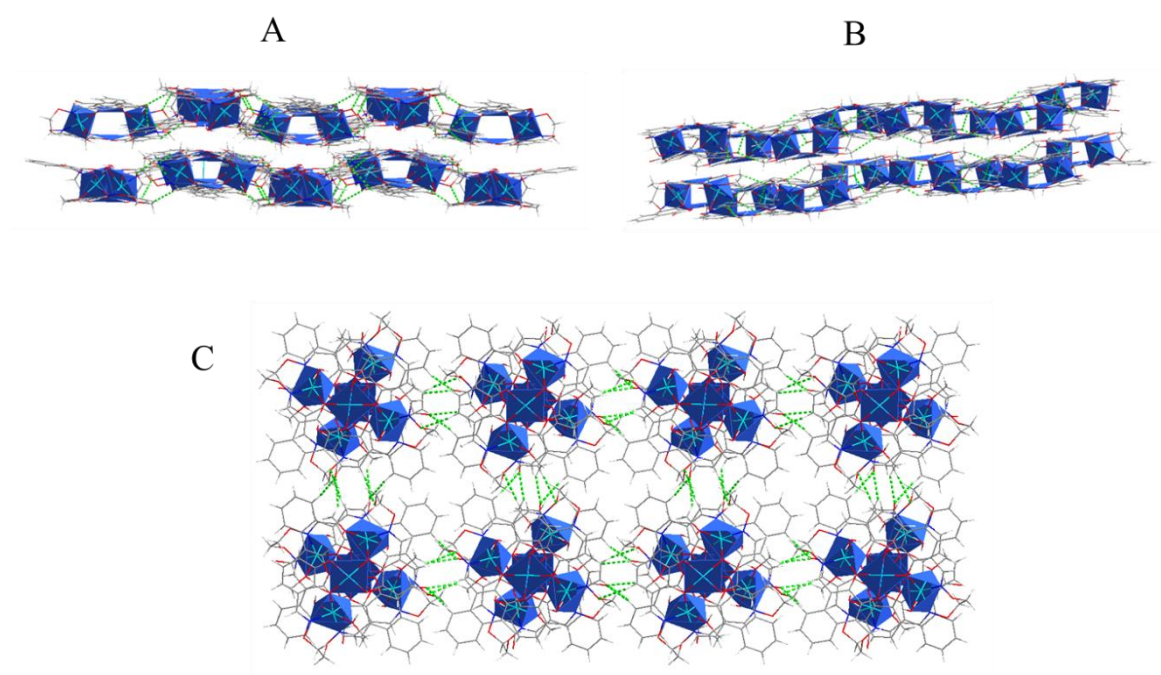


Fig. S5.

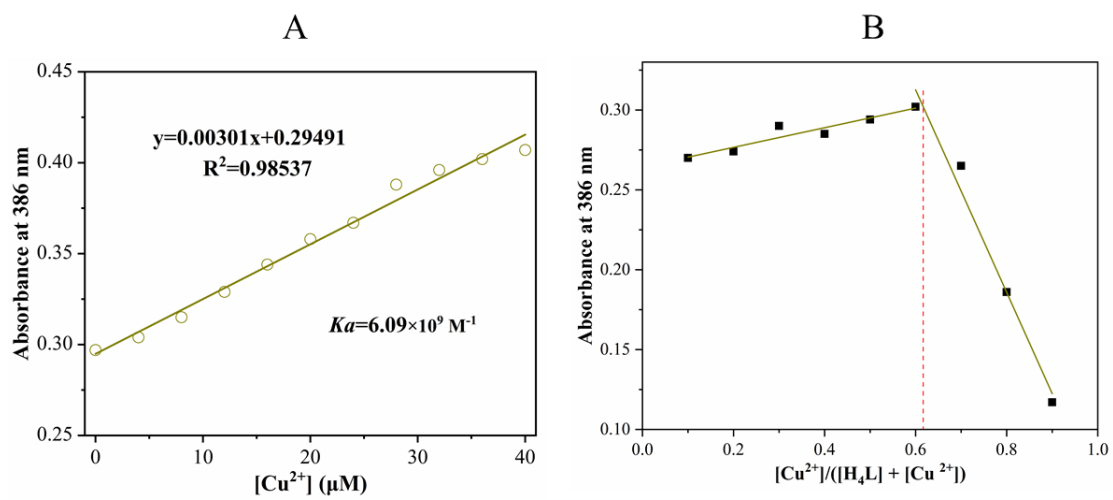
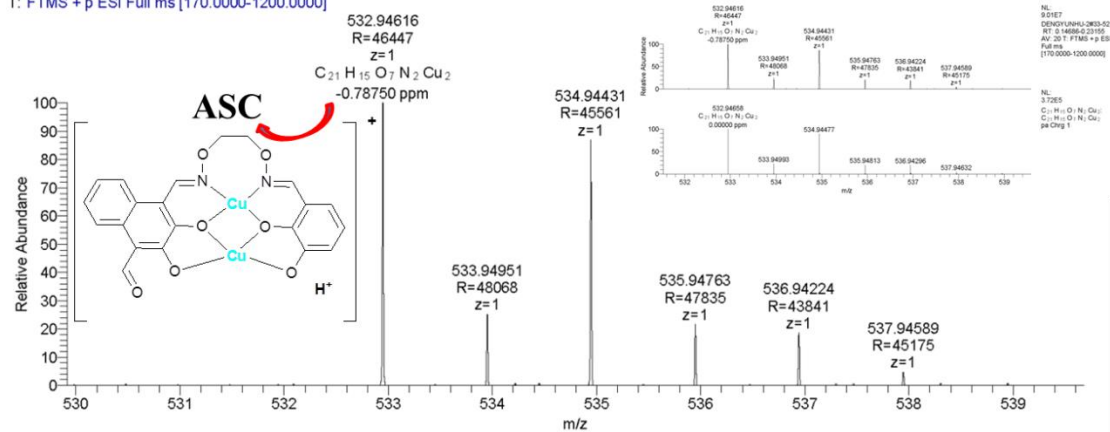


Fig. S6.

DENGYUNHU-2 #33-52 RT: 0.14686-0.23155 AV: 20 NL: 9.01E7
 T: FTMS + p ESI Full ms [170.0000-1200.0000]



DENGYUNHU-2#33-52 RT: 0.14686-0.23155 AV: 20
 T: FTMS + p ESI Full ms [170.0000-1200.0000]
 m/z= 529.91305-539.67724

m/z	Intensity	Relative	Resolution	Charge	Delta (ppm)	Composition
532.94616	93738960.0	100.00	46447.20	1.00	-0.79	C ₂₁ H ₁₅ O ₇ N ₂ Cu ₂
533.94951	22724348.0	24.24	48067.54	1.00		
534.94431	81287432.0	86.72	45561.34	1.00		
535.94763	19457640.0	20.76	47834.70	1.00		
536.94224	17100474.0	18.24	43841.02	1.00		

Fig. S7.

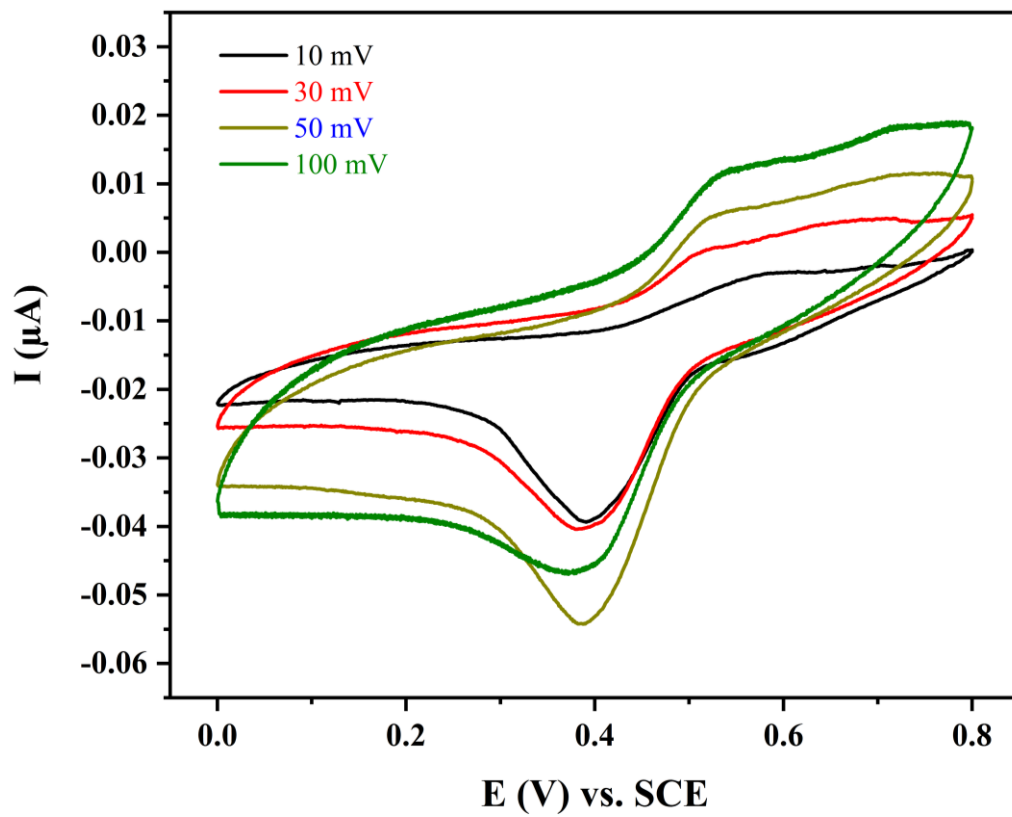


Fig. S8.

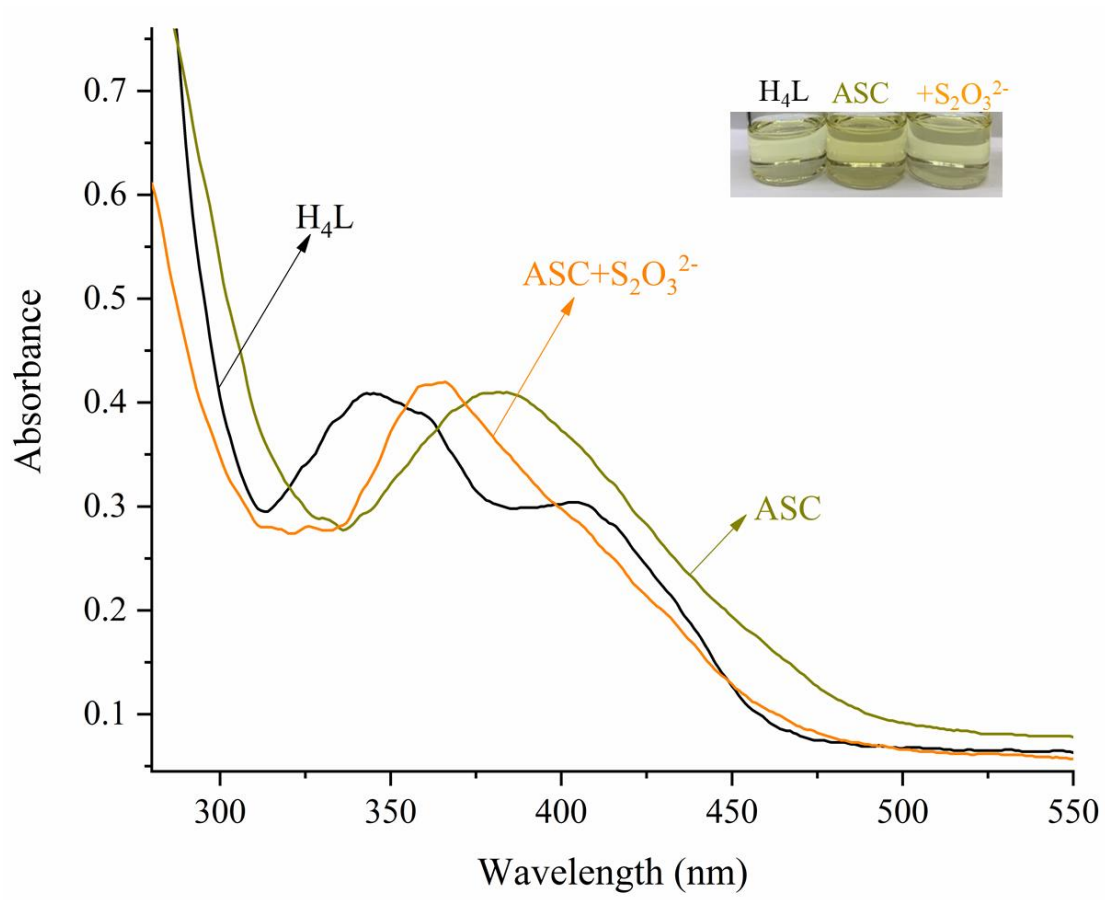


Fig. S9.

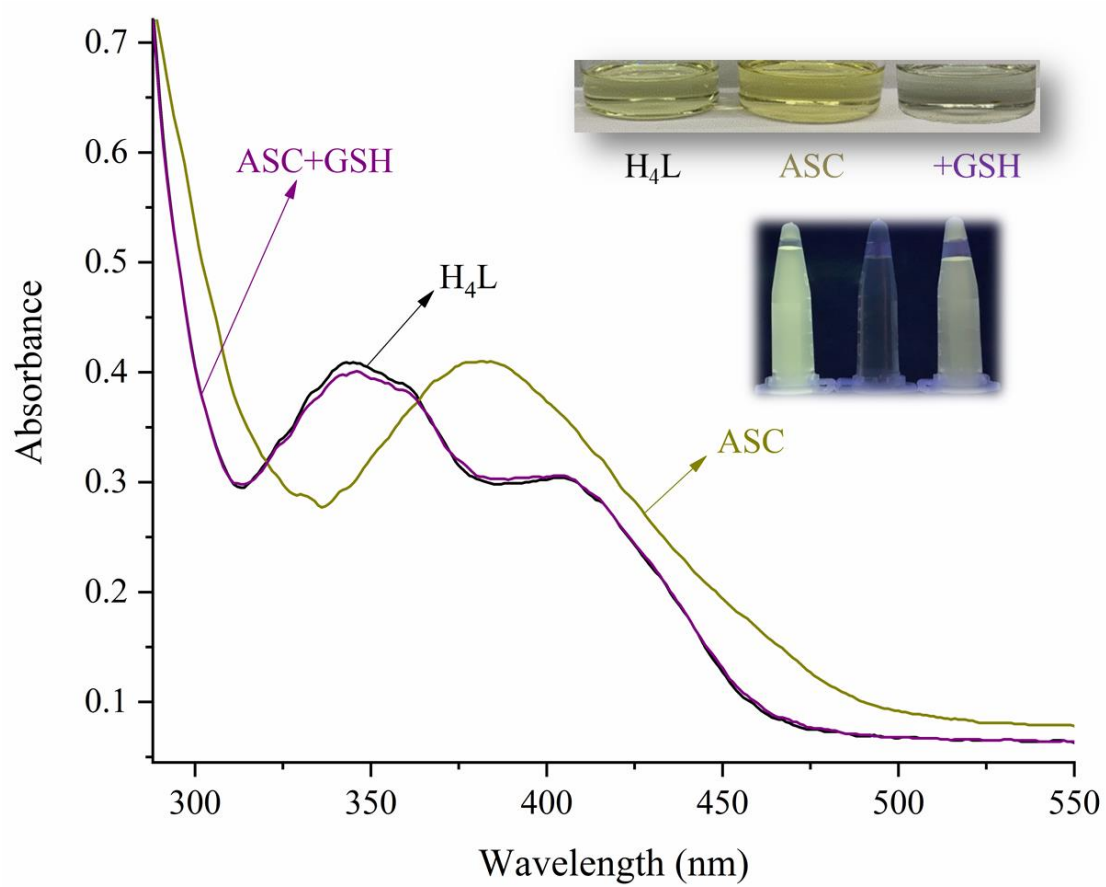


Fig. S10.

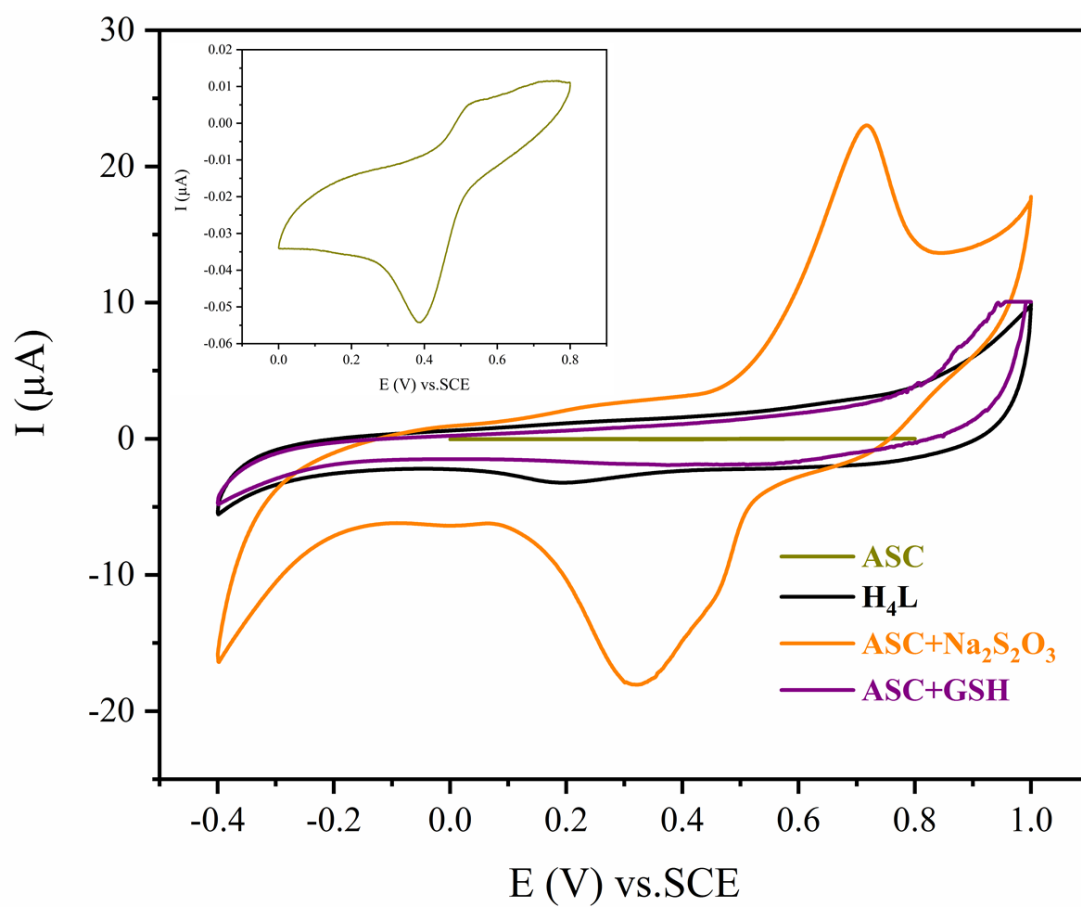


Fig. S11.

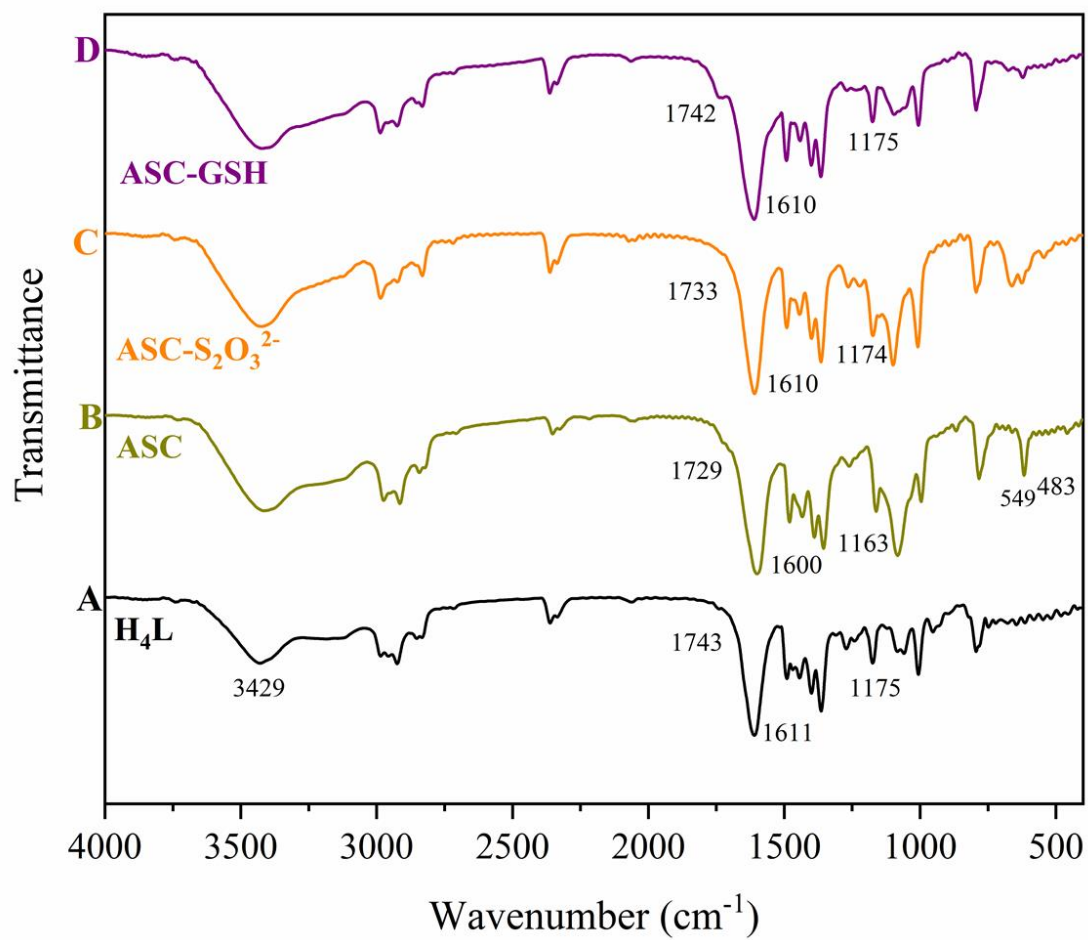
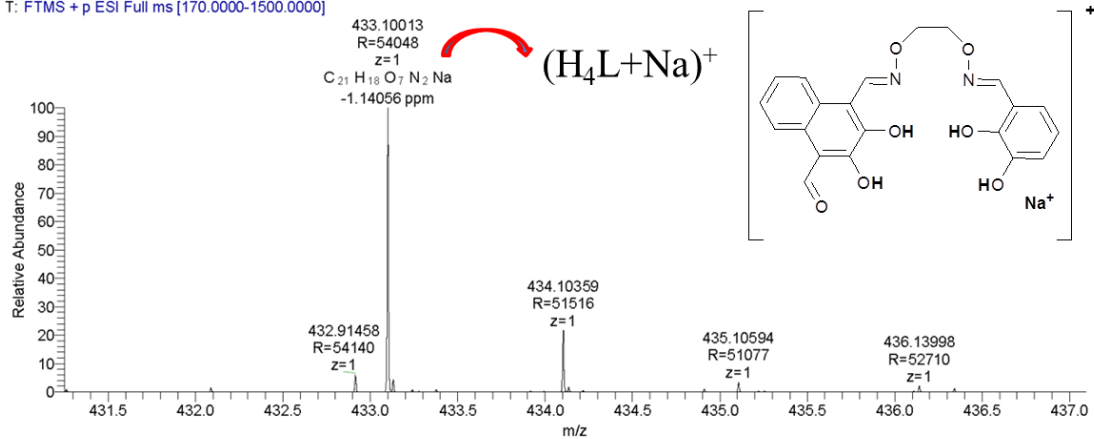


Fig. S12.

DENGYUNHU-4 #73-112 RT: 0.32497-0.49880 AV: 40 NL: 3.11E7
 T: FTMS + p ESI Full ms [170.0000-1500.0000]



DENGYUNHU-4 #73-112 RT: 0.32497-0.49880 AV: 40

T: FTMS + p ESI Full ms [170.0000-1500.0000]

m/z= 431.24908-437.09171

m/z	Intensity	Relative	Resolution	Charge	Delta (ppm)	Composition
432.91458	1887645.8	6.05	54139.69	1.00		
433.10013	31208302.0	100.00	54047.82	1.00	-1.14	C ₂₁ H ₁₈ O ₇ N ₂ Na
433.13078	1405823.8	4.50	54112.72	1.00		
434.10359	6929299.5	22.20	51516.05	1.00		
435.10594	1098762.4	3.52	51077.32	1.00		

Fig. S13.

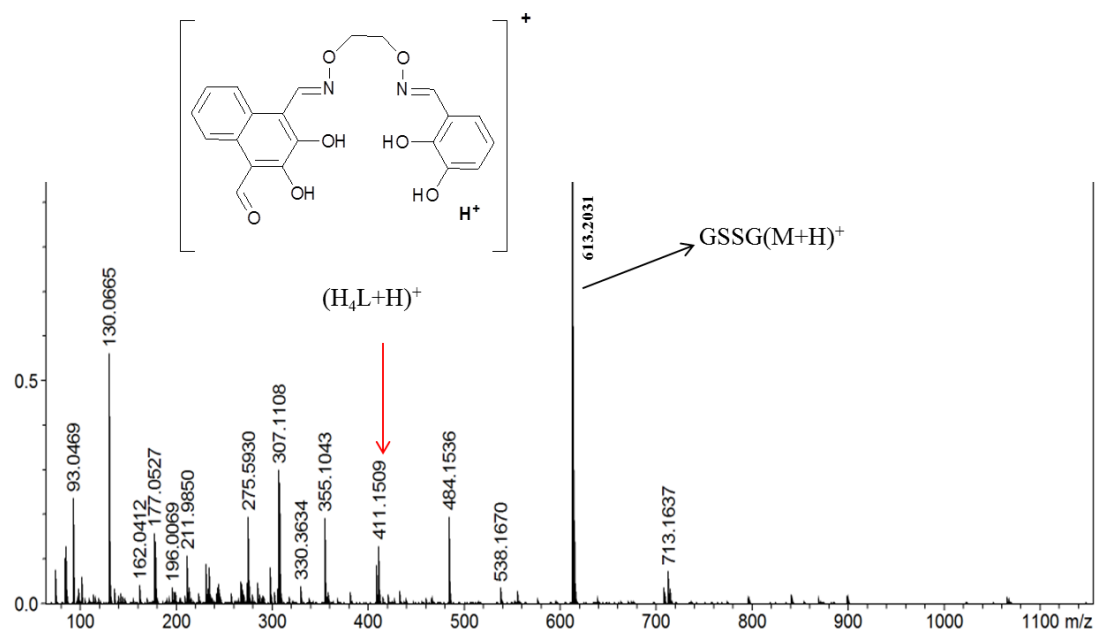


Fig. S14.

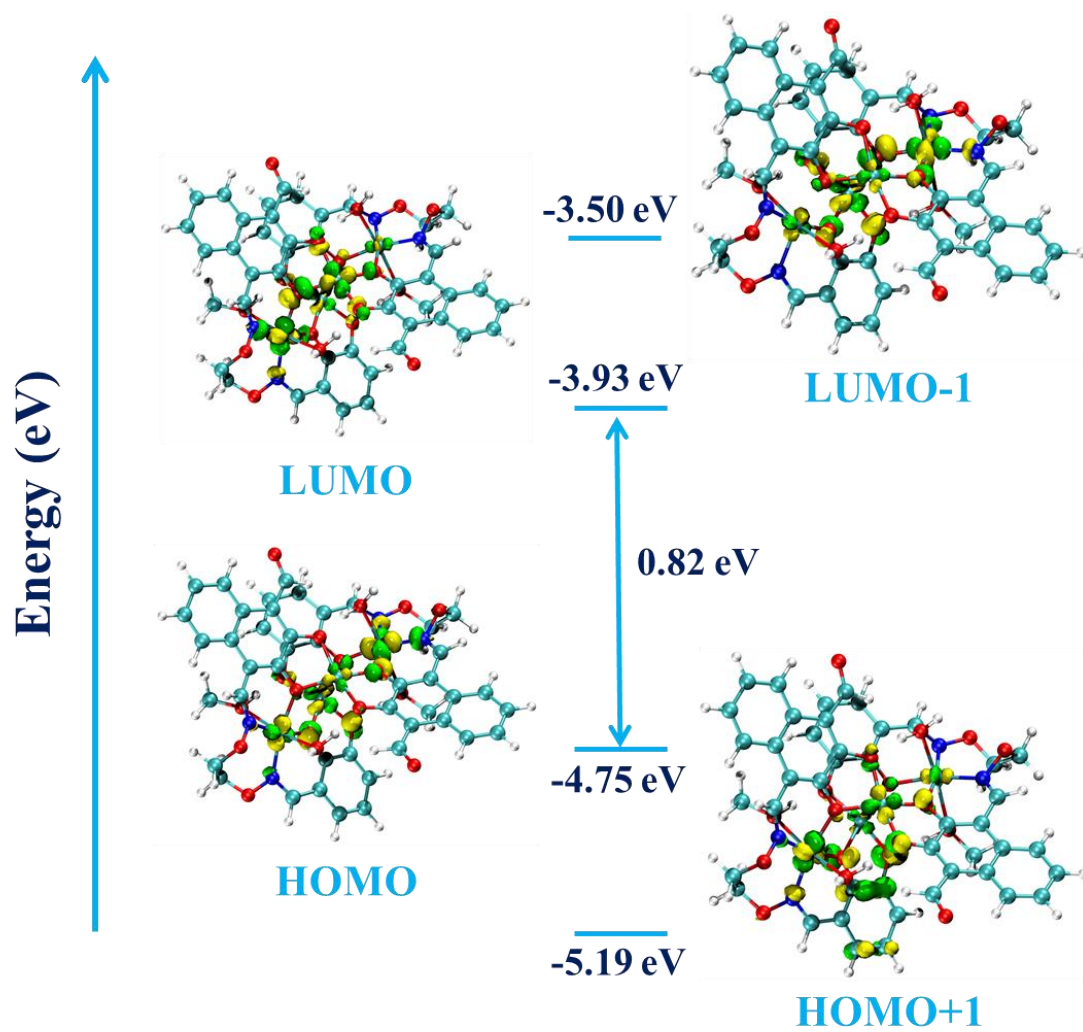


Fig. S15.

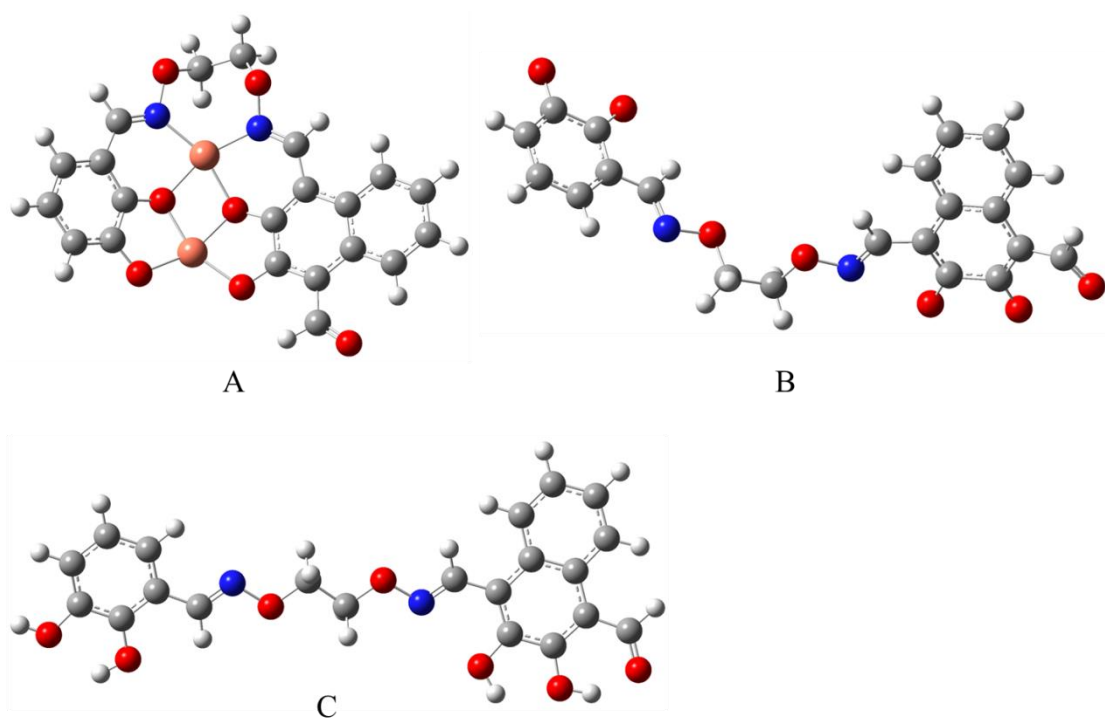


Fig. S16.

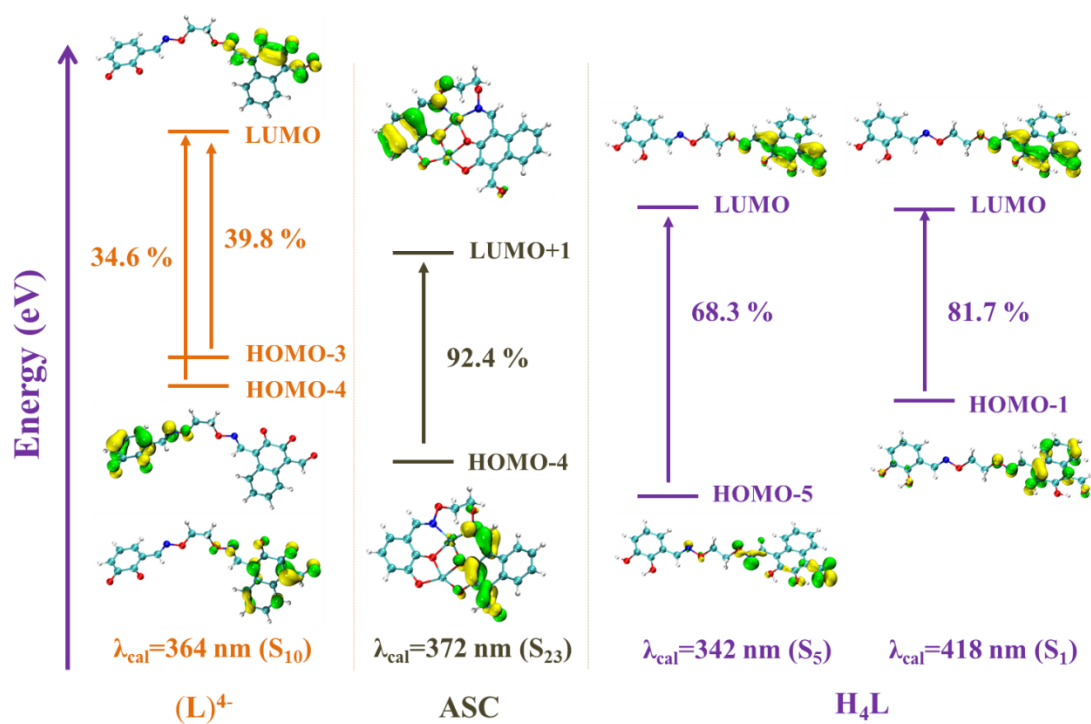


Fig. S17.

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