Electronic Supplementary Information

Stabilisation of copper(I) polypyridyl complexes toward aerobic oxidation by zinc(II) in combination with acetate anions: a facile approach and application in ascorbic acid sensing in aqueous solution

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Experimental Procedure

Ligand synthesis

2,2'-dipicolylamine (dpa). The **dpa** ligand was prepared according to a published procedure.[S1] To the suspension of anhydrous $MgSO_4$ (2.78 g, 23.1 mmol) in CH_2Cl_2 (3.80 mL) was added 2-pyridinecarboxaldehyde (0.50 g, 4.60 mmol) and 2-(aminomethyl)pyridine (0.50 g, 4.60 mmol). The mixture was stirred for 3 h at room temperature under N_2. After that, the suspension was filtered, and solvent in the filtrate was removed under vacuum to obtain a yellow-oil product. The product was redissolved in CH_3CN (12 mL) and cooled to -5°C for 15 min. The $NaBH_4$ was slowly added in the solution and stirred for 18 h at room temperature. The reaction was quenched with conc. HCl (7.70 mL) and heated at 60°C for 2 h to give the white precipitates in yellow solution. The white solid was filtered out, and solvent in the filtrate was removed under vacuum. The crude product was redissoved in H_2O. To the aqueous solution was added NaOH pellets (3.30 g, 82.5 mmol) and the mixture was stirred for 15 min. The solution was extracted with diethyl ether (3 x 200 mL) and dried under vacuum to obtain the yellow oil product. Yield: 80 %. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.49 (m, 2H, Ar*H*), 7.50 (m, 2H, Ar*H*), 7.23 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.01 (m, 2H, Ar*H*), 3.84 (s, 4H, -CH_2-).

2-[bis(2-pyridylmethyl)aminomethyl]nitrobenzene. This ligand was prepared by following a modified published procedure.[S2] The mixture solution of **dpa** (3.86 g, 19.37 mmol), 2-nitrobenzylbromide (4.19 g, 19.40 mmol) and molecular sieve (5 g) was prepared in CH_3CN (80 mL). The reaction was stirred at room temperature under N_2 for 16 h. The suspension was filtered, and the organic solvent was evaporated. Then, the crude product was redissolved in CH_2Cl_2 and washed with H_2O (3 x 300 ml). The organic layer was dried with anhydrous $NaSO_4$, and the solvent was removed to obtain a dark-brown oil. Yield: 80 %. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.49 (d, 2H, *J* = 4.4 Hz, Ar*H*), 7.75 (m, 1H, Ar*H*), 7.70 (dd, 1H, *J* = 0.5, 7.5 Hz, Ar*H*), 7.64 (td, 2H, *J* = 6 Hz ,Ar*H*), 7.49 (t, 1H, *J* = 7.2 Hz, Ar*H*), 7.39 (d, 2H, *J* = 7.6 Hz, Ar*H*), 7.33 (t, 1H, *J* = 7.6 Hz, Ar*H*), 7.13 (m, 2H, Ar*H*), 4.07 (s, 2H, -CH_2-), 3.79 (s, 4H,-CH_2-).

2-[bis(2-pyridylmethyl)aminomethyl]aniline (tpa). The **tpa** was prepared following a modified published procedure.[S2] Into a 2-[bis(2-pyridylmethyl)aminomethyl]nitrobenzene (3 g, 8.97 mmol) in two-neck round bottom flask, Pd-C (0.3 g) and MeOH (150 ml) were added and stirred under H_2 for 24 h. The mixture was filtered through celite and the solvent was removed under reduced pressure. Yield: 98%, red brown oil. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.56 (m, 2H, Ar*H*), 7.62 (m, 2H, Ar*H*), 7.36 (d, 2H, *J* = 7.2 Hz, Ar*H*), 7.16 (m, 2H, Ar*H*), 7.07 (m, 2H, Ar*H*), 6.63 (t, 2H, *J* = 6.0 Hz, Ar*H*), 3.82 (s, 4H, -CH_2-), 3.71 (s, 2H, -CH_2-).

9-[(2,2'-dipicolylamino)methyl]anthracene (adpa). The ligand **adpa** was synthesized according to a published method.[S3] The stirred solution of 9-bis(chloromethyl)anthracene (1.00 g, 4.40 mmol), 2,2'-dipicolylamine (1.05 g, 5.20 mmol) and K_2CO_3 (2.43 g, 1.70 mmol) in anhydrous DMF (6.8 mL) was slowly added a solution of KI (0.73 g, 4.40 mmol) in DMF (3.6 mL). The reaction was stirred at room temperature over 1 h. To the reaction was added 1M HCl, and the solution was washed with EtOAc (3X). Then, the aqueous solution was alkalized with 4 M NaOH and extracted by EtOAc : THF (1 : 1).

The organic layer was washed with H_2O and brine solution. The solution was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The product was obtain after crystallization in MeOH : ether. Yield: 27%, a pale yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.49 (d, 2H, *J* = 4.0 Hz, Ar*H*), 8.39 (s, 1H, Ar*H*), 8.37 (d, 2H, *J* = 4.8 Hz, Ar*H*), 7.95 (m, 2H, Ar*H*), 7.57 (ddd, 2H, *J* = 1.6, 7.6, 7.6 Hz, Ar*H*), 7.41-7.47 (m, 4H, Ar*H*), 7.31 (d, 2H, *J* = 7.6 Hz, Ar*H*), 7.11 (dd, 2H, *J* = 4.8, 6.0 Hz, Ar*H*), 4.67 (s, 2H, -CH_2-), 3.88 (s, 4H, -CH_2-).

N-(anthracene-9-yl methyl)-2-(((pyridin-2-ylmethyl)(pyridin-3-yl methyl)amino)methyl)aniline (atpa). The ligand **atpa** was synthesized following a reported procedure.[S4] **atpa** was prepared from reaction of **tpa** (1.50 g, 4.92 mmol) and anthracene-9-carbaldehyde (1.02 g, 4.95 mmol). The mixture solution of **tpa** and anthracene-9-carbaldehyde in CH_3CN (106 mL) was refluxed under N_2 atmosphere for 24 h. The mixture was evaporated under reduced pressure to obtain the imine product. After that, the imine was reduced by $NaBH_4$ (0.68 g) in MeOH at low temperature and further refluxed for 16 h. H_2O was added into the solution, and then the MeOH was removed under reduced pressure. The aqueous solution was extracted with CH_2Cl_2 and evaporated. The crude product was purified by column chromatography and then recrystallized in MeOH : ether (1 : 3). Yield: 20%, a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.59 (s, 1H, Ar*H*), 8.20 (dd, 4H, *J* = 49.6, 8.8 Hz, Ar*H*), 8.02 (d, 2H, *J* = 7.2 Hz, Ar*H*), 7.51 (dt, 4H, *J* = 33.6, 7.6 Hz, Ar*H*), 7.34 (t, 1H, *J* = 7.6 Hz, Ar*H*), 7.08 (dd, 2H, *J* = 43.0, 7.8 Hz, Ar*H*), 6.73 (m, 3H, Ar*H*), 6.59 (td, 2H, *J* = 7.6, 1.6 Hz, Ar*H*), 6.41 (d, 2H, *J* = 7.6 Hz, Ar*H*), 6.07 (bs, 1H, N*H*), 5.12 (d, 2H, *J* = 4.0 Hz, -CH_2-), 3.54 (s, 2H, -CH_2-), 3.48 (s, 4H, -CH_2-).

Synthesis of copper complexes

Cu^{II}(adpa) was synthesized according to a published procedure.[S5] To a solution of **adpa** (0.15 g, 0.39 mmol) in MeOH (3 mL) was added $Cu(ClO_4)_2$ (0.16 g, 0.43 mmol) dissolved in MeOH (3 mL). After stirred for 2h, diethyl ether was added into the solution to crystallize the green solid of Cu^{II}(**adpa**)**.** (61 % yield). Anal. Calcd (found) of $C_{27}H_{25}Cl_2CuN_3O_9$: %C = 48.40 (48.09), %H = 3.76 (3.74), %N = 6.27 (6.32). ESI-MS (*m/z*) of [Cu(**adpa**)+(ClO_4)]$^+$ for calculated: 551.07; found: 551.0676.

Cu^{II}(atpa) was synthesized from **atpa** and $Cu(ClO_4)_2$. To a stirred solution of **atpa** (0.10 g, 0.20 mmol) in CH_2Cl_2, $Cu(ClO_4)_2$ (0.11 g, 0.30 mmol) in MeOH was added. The reaction was stirred for 2 h to obtain the blue-green solid of Cu^{II}(**atpa**). Next, the solid was filtered and washed with CH_2Cl_2 and MeOH. (85 % yield). Anal. Calcd (found) of $C_{34}H_{32}Cl_2CuN_4O_9$: %C = 52.69 (52.63), %H = 4.16 (4.12), %N = 7.23 (7.14). ESI-MS (*m/z*) of Cu(**atpa**), [Cu(**atpa**)+(ClO_4)]$^+$ for calculated: 656.13; found: 656.0957.

References

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(S2) S. C. Burdette, C. J. Frederickson, W. Bu and S. J. Lippard, *J. Am. Chem. Soc.*, 2003, **125**, 1778-1787.

(S3) A. Ojida, Y. Mito-oka, M.-a. Inoue and I. Hamachi, *J. Am. Chem. Soc.*, 2002, **124**, 6256-6258.

(S4) U. Khamjumphol, S. Watchasit, C. Suksai, W. Janrungroatsakul, S. Boonchiangma, T. Tuntulani and W. Ngeontae, *Anal. Chim. Acta*, 2011, **704**, 73-86.

(S5) B. Antonioli, B. Buchner, J. K. Clegg, K. Gloe, K. Gloe, L. Gotzke, A. Heine, A. Jager, K. A. Jolliffe, O. Kataeva, V. Kataev, R. Klingeler, T. Krause, L. F. Lindoy, A. Popa, W. Seichter and M. Wenzel, *Dalton Trans*, 2009, 4795-4805.

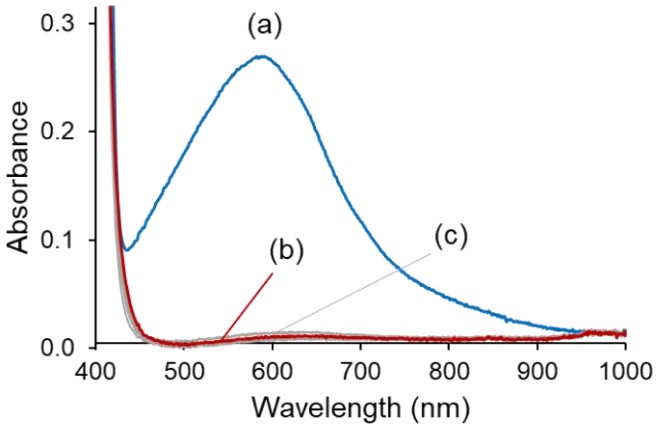


Fig. S1 UV-vis spectra of (a) Cu^{II}(**adpa**) (2.0 mM) in CH_3CN; (b) Cu^{II}(**adpa**) upon addition of AsH_2 (0.55 mol equiv.) and (c) b after purging O_2 1-5 h

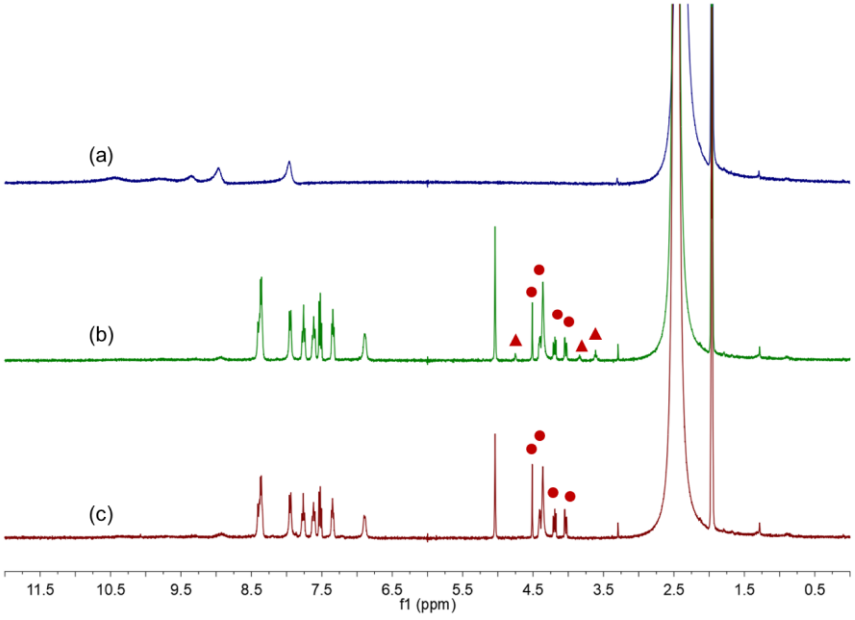


Fig. S2 ^{1}H-NMR spectra of (a) 10 mM Cu^{II}(**adpa**) in CD_3CN; (b) a + AsH_2 (0.55 mol equiv.) in 15% D_2O/CD_3CN; and (c) b exposed to air for 1 h at room temperature. ^{1}H-NMR signals (▲) belong to AsH_2, whereas (●) correspond to a bicyclic form of dehydroascorbic acid (oxidized form of ascorbic acid)

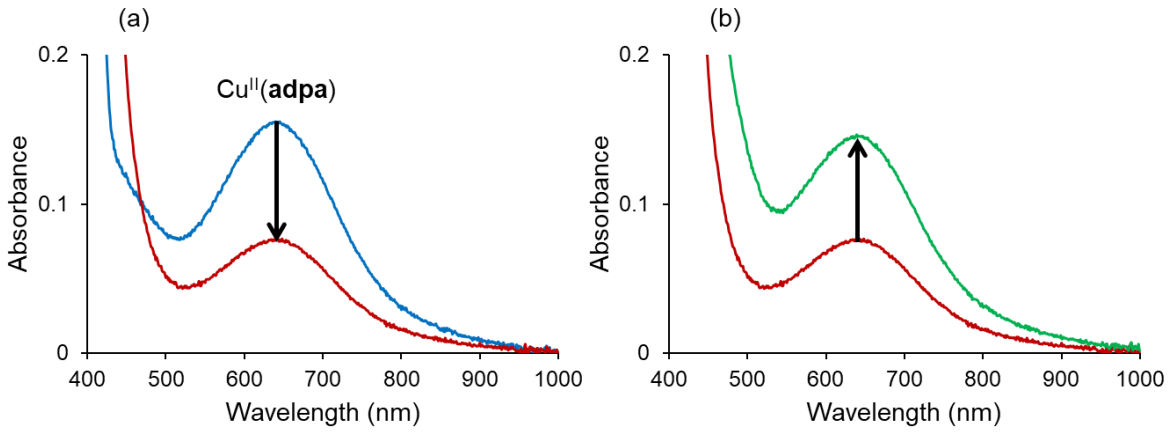


Fig. S3 Monitoring *d-d* band of Cu^{II}(**adpa**) in H_2O/CH_3CN (7:3 v/v) at (a) 2 min; and (b) 2 h after addition of AsH_2 (1.0 mol equiv.) in air

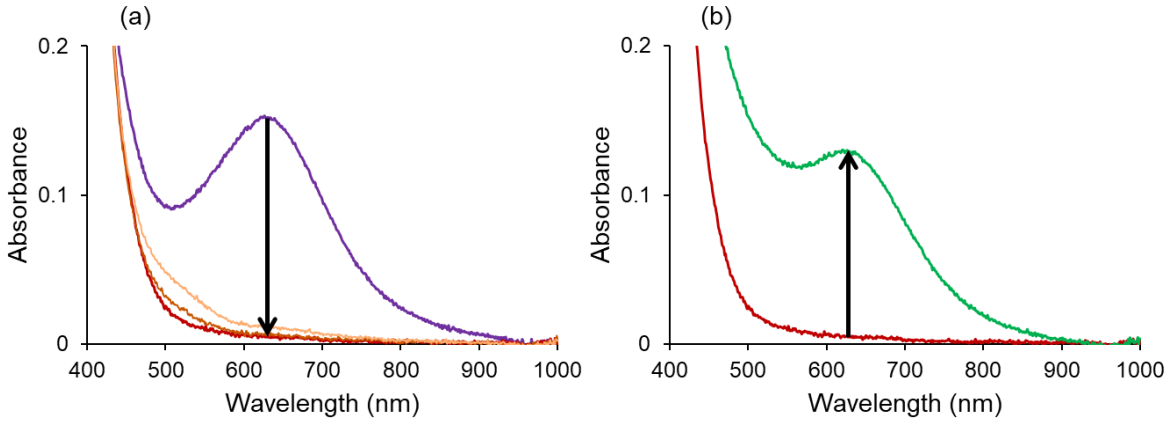


Fig. S4 (a) Monitoring the reaction of Cu^{II}(**adpa**) and AsH_2 in the presence of $Zn(OAc)_2$ in aqueous solution: 2 min (—), 30 min (—) and 60 min (—) after AsH_2 addition; (b) Regeneration of Cu^{II}(**adpa**) after exposed to air for 4 h (—)

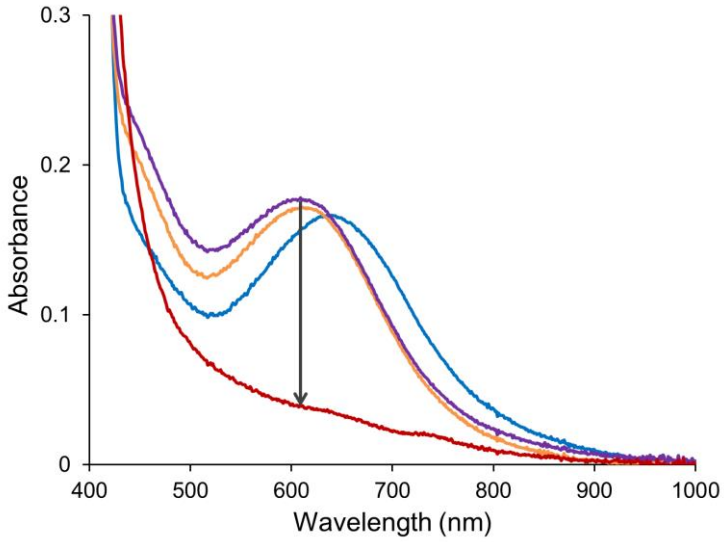


Fig. S5 UV-vis spectra of Cu^{II}(**adpa**) (——) in the presence of imidazole (——) and $Zn(NO_3)_2$ (——) upon addition of AsH_2 1 mol equiv. (——)

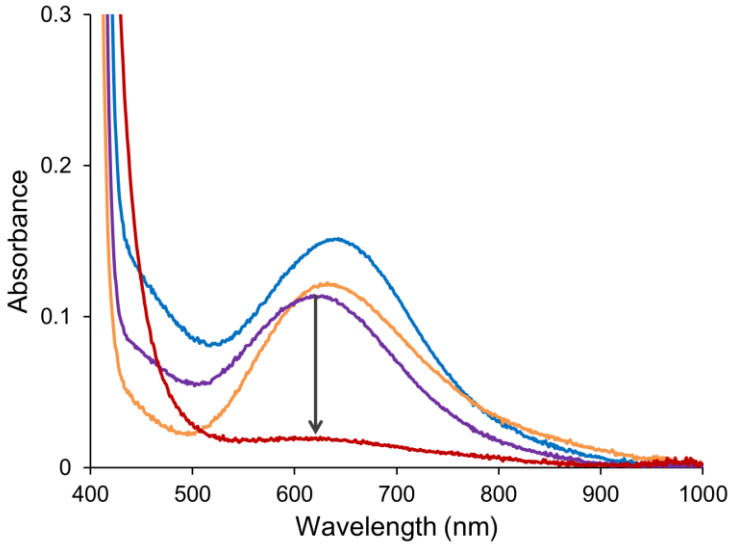


Fig. S6 UV-vis spectra of Cu^{II}(**adpa**) (——) in the presence of histidine (——) and $Zn(NO_3)_2$ (——) upon addition of AsH_2 1 mol equiv. (——)

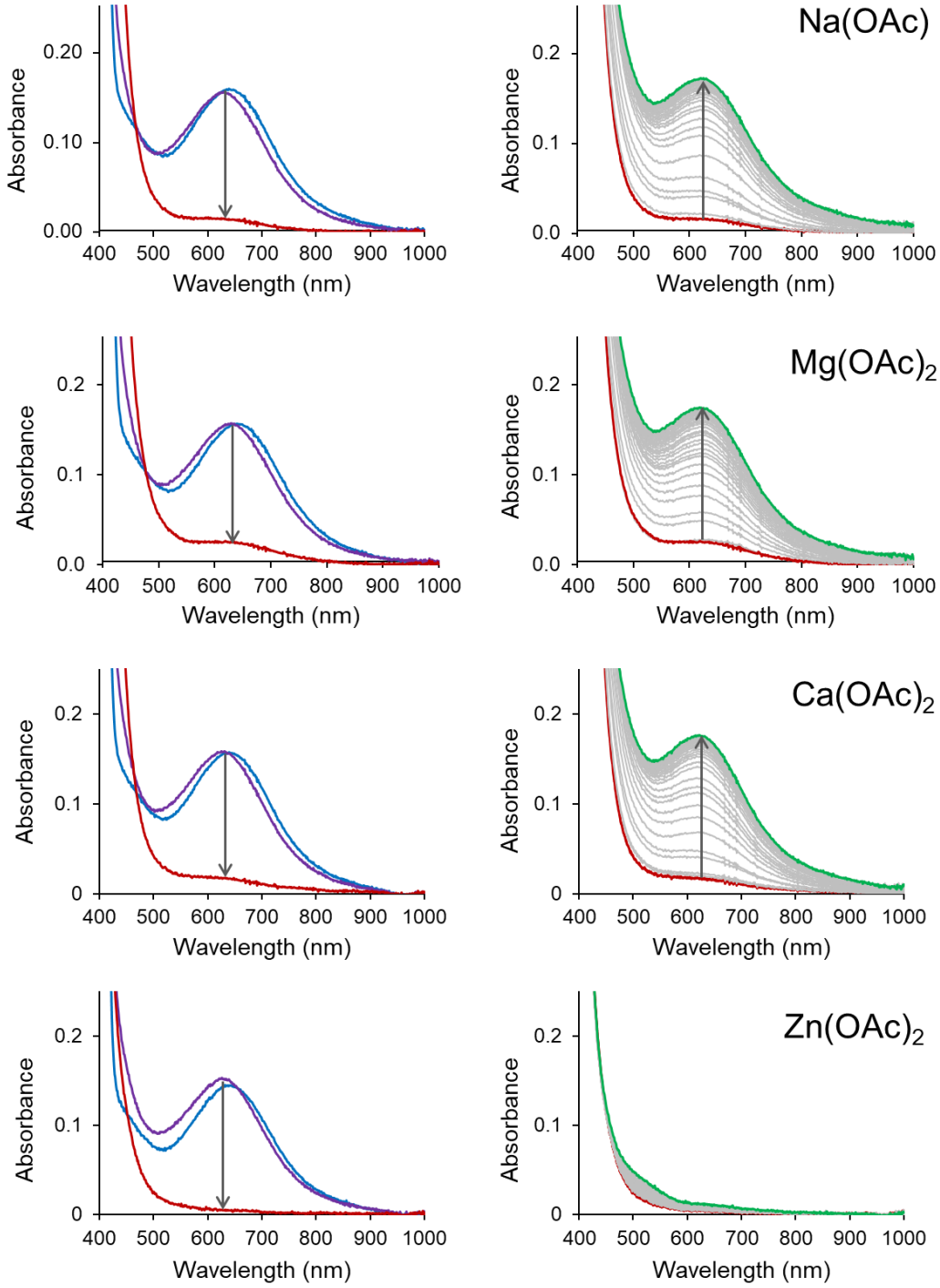


Fig. S7 UV-Vis spectral change for reaction of Cu^{II}(**adpa**) and AsH_2 (1.0 equiv) in the presence of Na(OAc), $Mg(OAc)_2$, $Ca(OAc)_2$ and $Zn(OAc)_2$ in H_2O/CH_3CN (7:3 v/v) under aerobic condition. The coloured line corresponds to species as follows; Cu^{II}(**adpa**) (—), Cu^{II}(**adpa**)+$M(OAc)_n$ (—), Cu^{II}(**adpa**)+$M(OAc)_n$+AsH_2 under aerobic condition at 2 min (—), between 2-60 min (—) and 60 min (—)

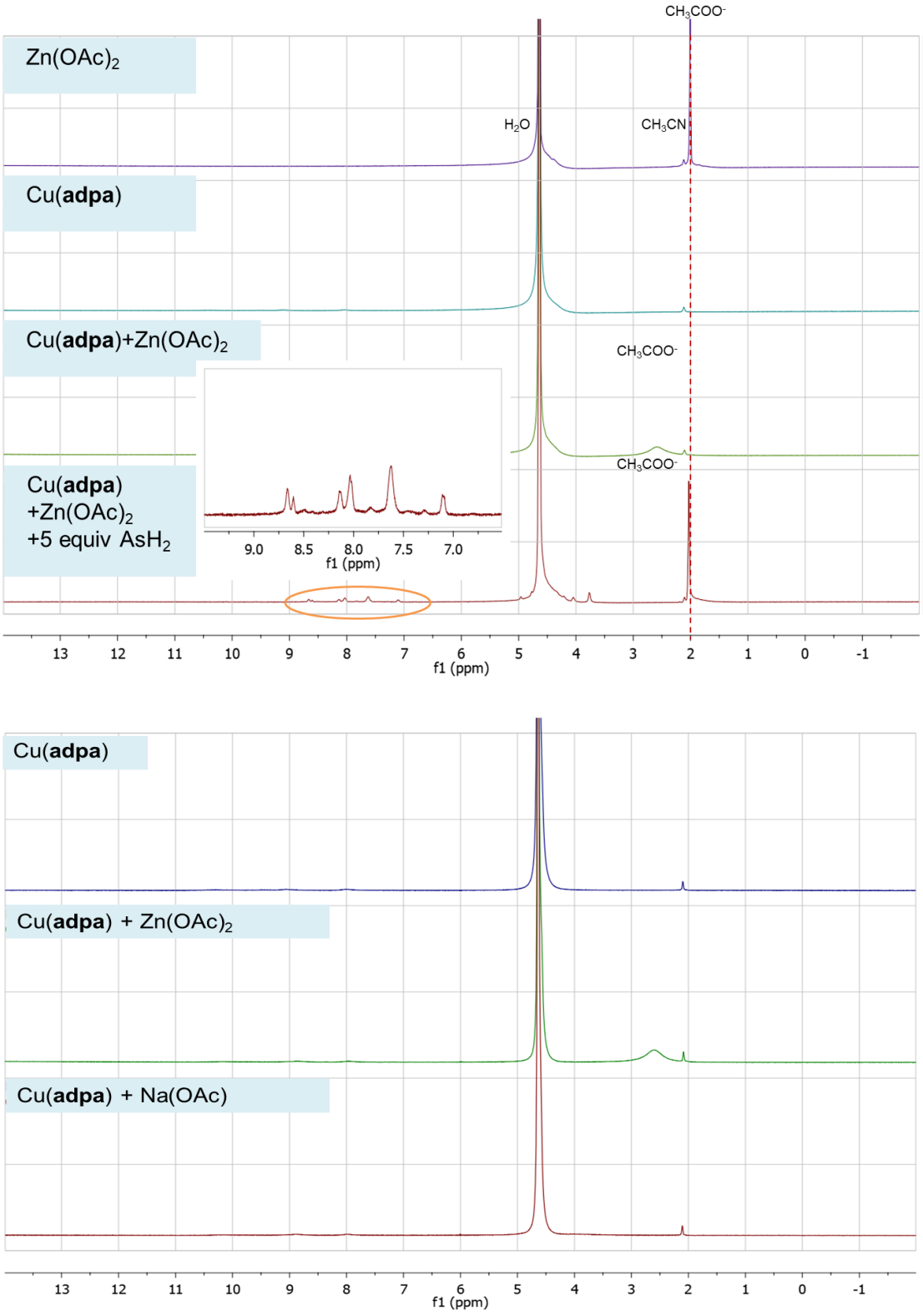


Fig. S8 Comparison of ^{1}H-NMR signals corresponding to acetate anions in various conditions

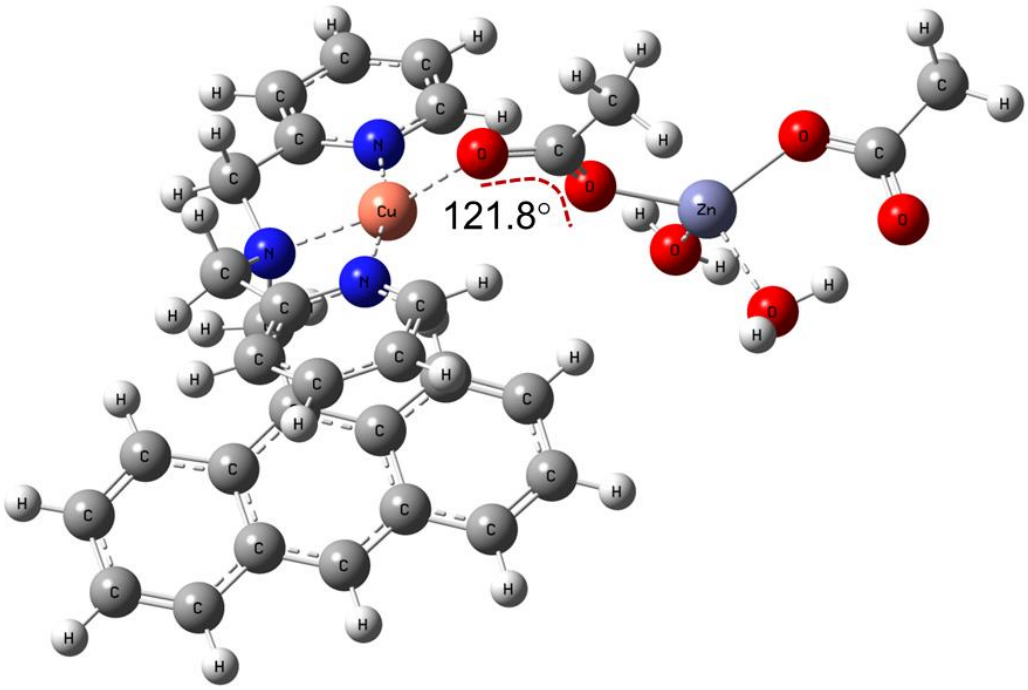


Fig. S9 The CPCM(UFF)/B3LYP/6–311+G(d,p)–optimised structure of Cu^{II}(**adpa**)/$Zn(OAc)_2(H_2O)_2$ complex.

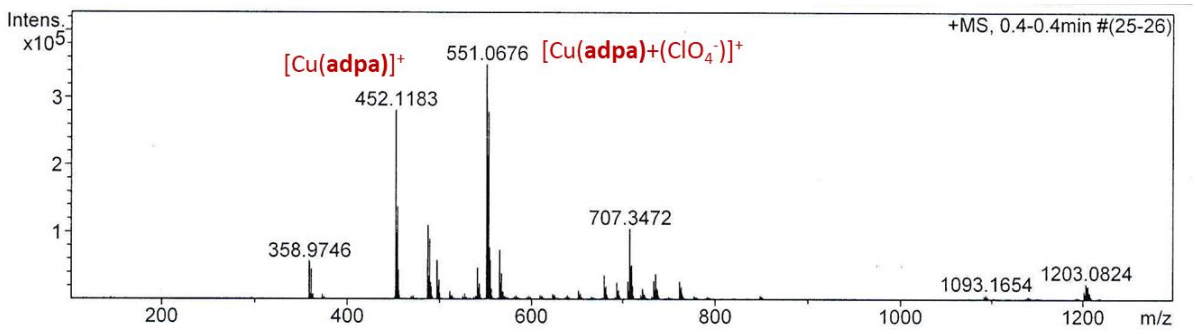


Fig. S10 ESI-MS spectrum of Cu^{II}(**adpa**) in H_2O/CH_3CN (7:3 v/v).

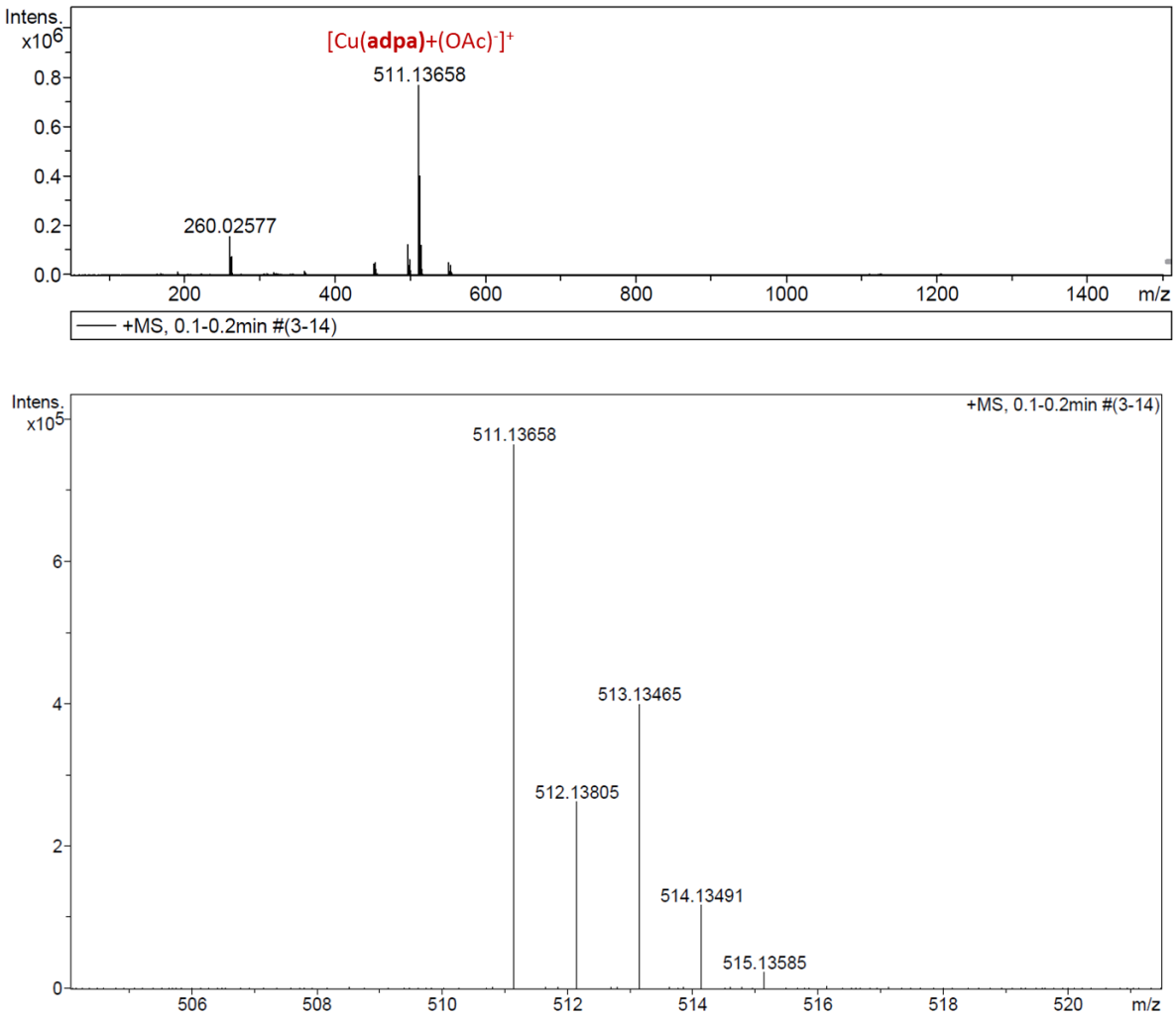


Fig. S11 ESI-MS spectrum of Cu^{II}(**adpa**) in the presence of $Zn(OAc)_2$ in H_2O/CH_3CN (7:3 v/v).

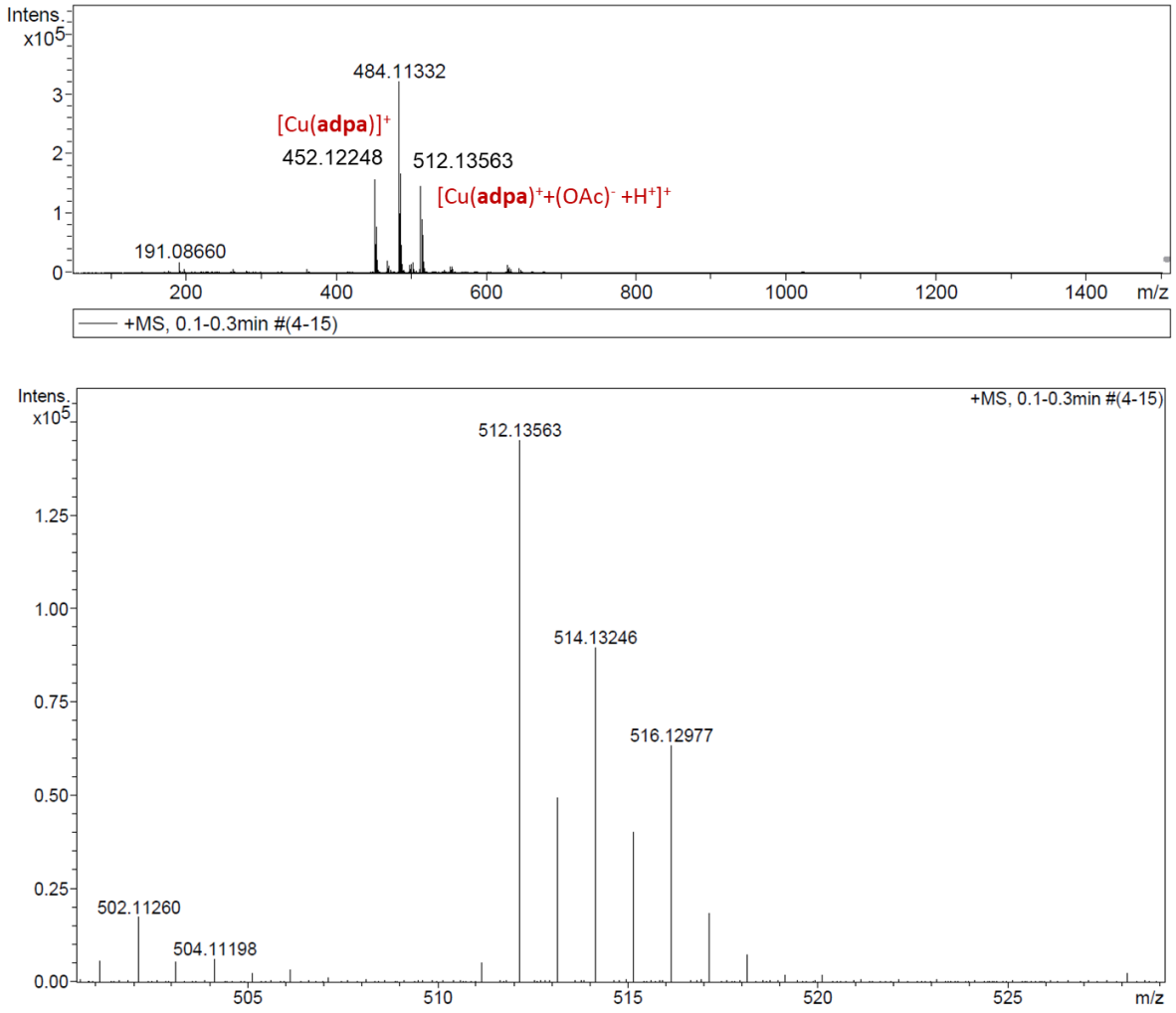


Fig. S12 ESI-MS spectrum of the reaction of Cu^{II}(**adpa**) + $Zn(OAc)_2$ + AsH_2 (5 mol equiv.) H_2O/CH_3CN (7:3 v/v).

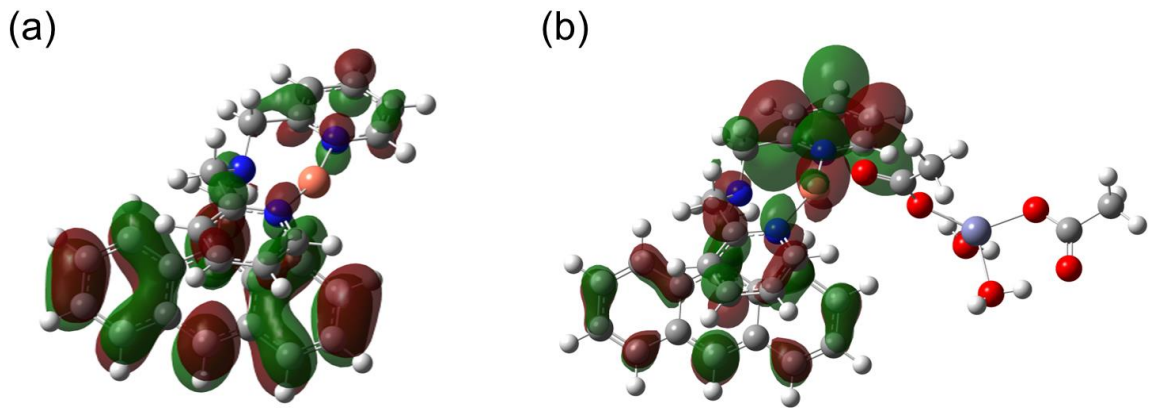


Fig. S13 LUMOs plots of (a) Cu^{I}(**adpa**) and (b) Cu^{I}(**adpa**)/$Zn(OAc)_2(H_2O)_2$, computed at the CPCM(UFF)/B3LYP/6–311+G(d,p) level of theory.

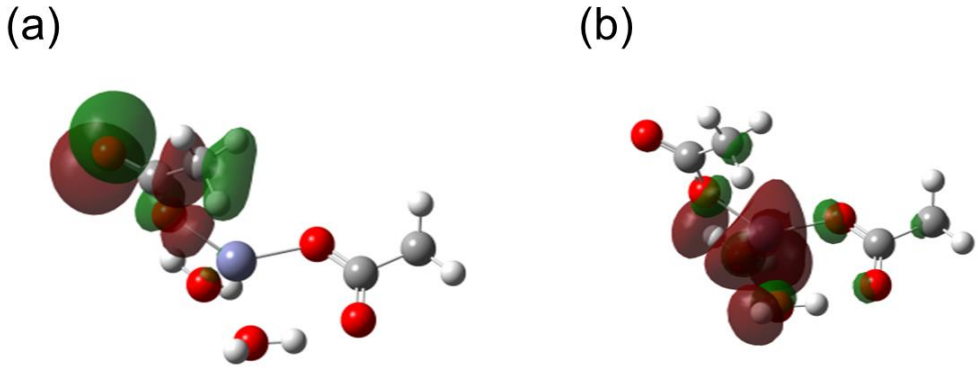


Fig. S14 Plots of (a) HOMO and (b) LUMO of the $Zn(OAc)_2(H_2O)_2$ complex, computed at the CPCM(UFF)/B3LYP/6–311+G(d,p) level of theory.

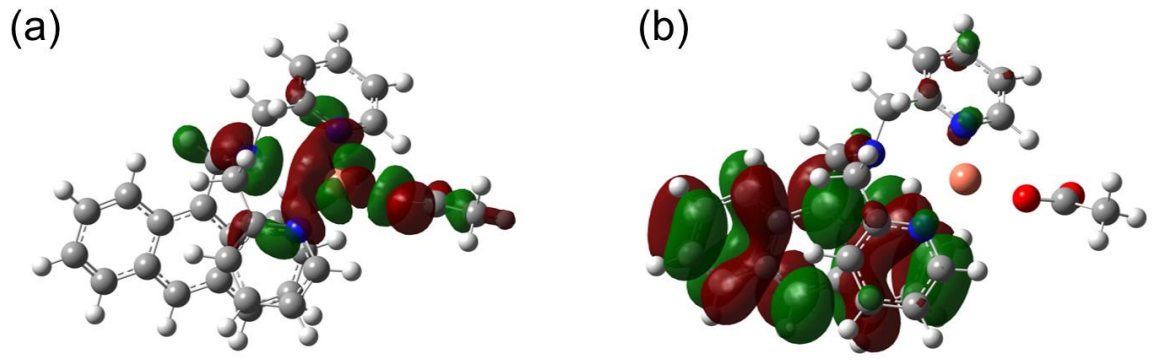


Fig. S15 Plots of (a) HOMO and (b) LUMO of the Cu^{I}(**adpa**)/(OAc^{-}) complex, computed at the CPCM(UFF)/B3LYP/6–311+G(d,p) level of theory.

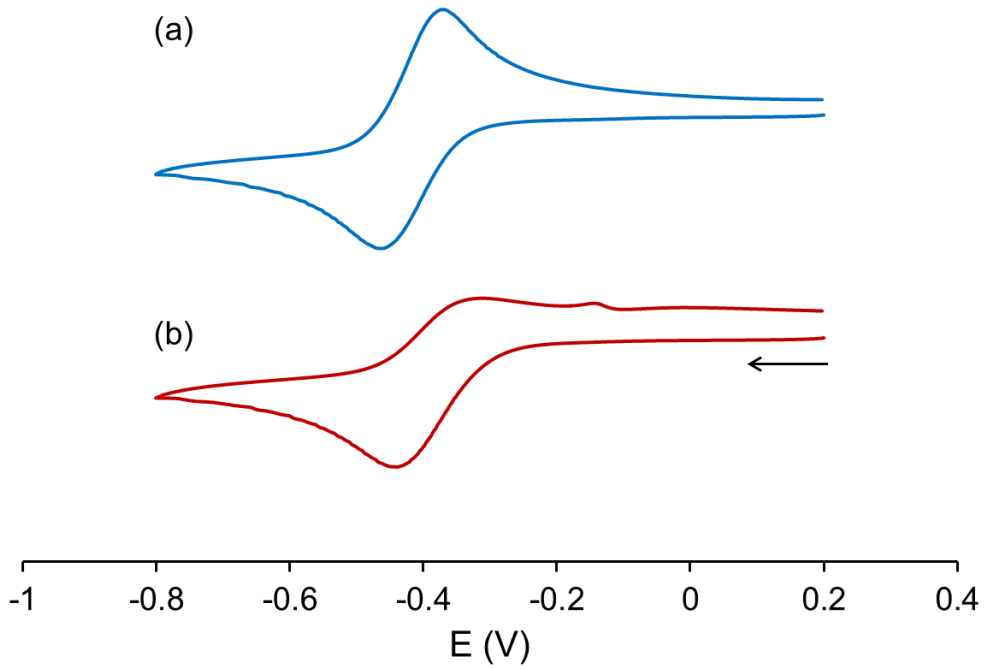


Fig. S16 Cyclic voltammogram of (a) Cu^{II}(**adpa**) (1.0 mM) and (b) Cu^{II}(**adpa**)+$Zn(OAc)_2$ (8 mol equiv.) in H_2O/CH_3CN (7:3 v/v) with 0.1 M ABS buffer (pH 5.6) at scan rate = 100 mV/s.

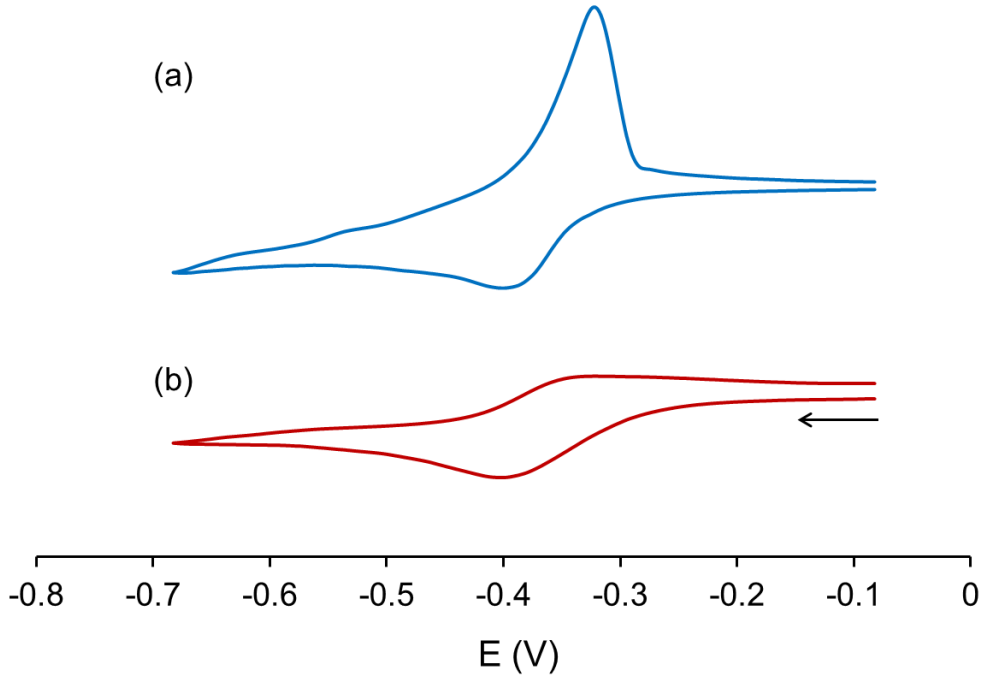


Fig. S17 Cyclic voltammogram of (a) Cu^{II}(**adpa**) (1.0 mM) and (b) Cu^{II}(**adpa**)+$Zn(OAc)_2$ (8 mol equiv.) in H_2O/CH_3CN (7:3 v/v) with 0.1 M KPF_6 at scan rate = 100 mV/s.

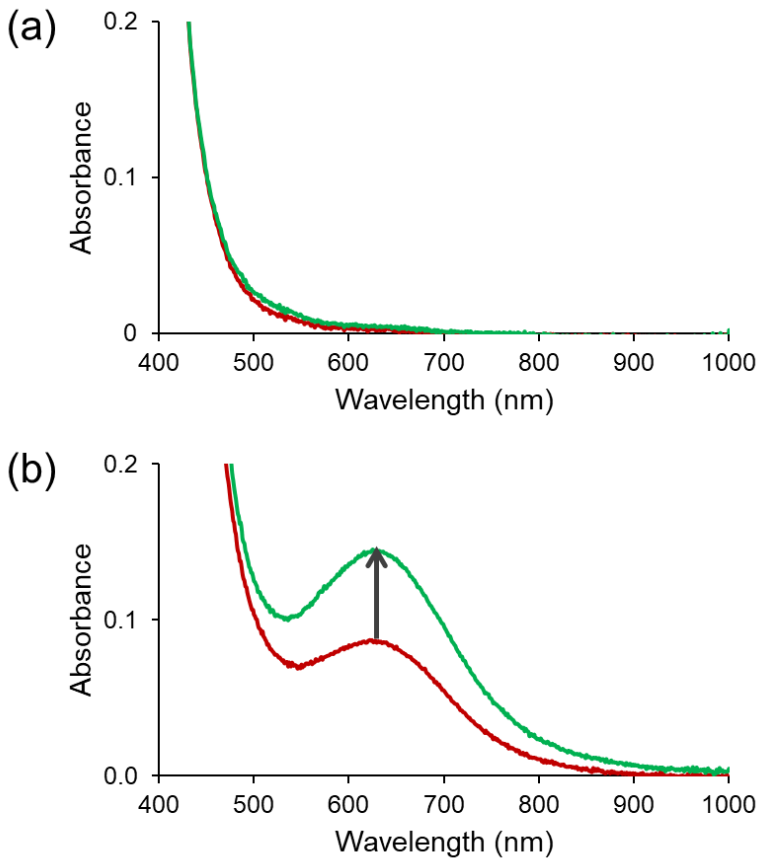


Fig. S18 UV-vis spectral change at *d*-*d* band of Cu(**adpa**) with AsH_2 (1 mol equiv.) in H_2O/CH_3CN (7:3 v/v) buffered with ABS at pH 5.6 (a) in the presence and (b) absence of $Zn(OAc)_2$ at 2 min (—) and 20 min (—)

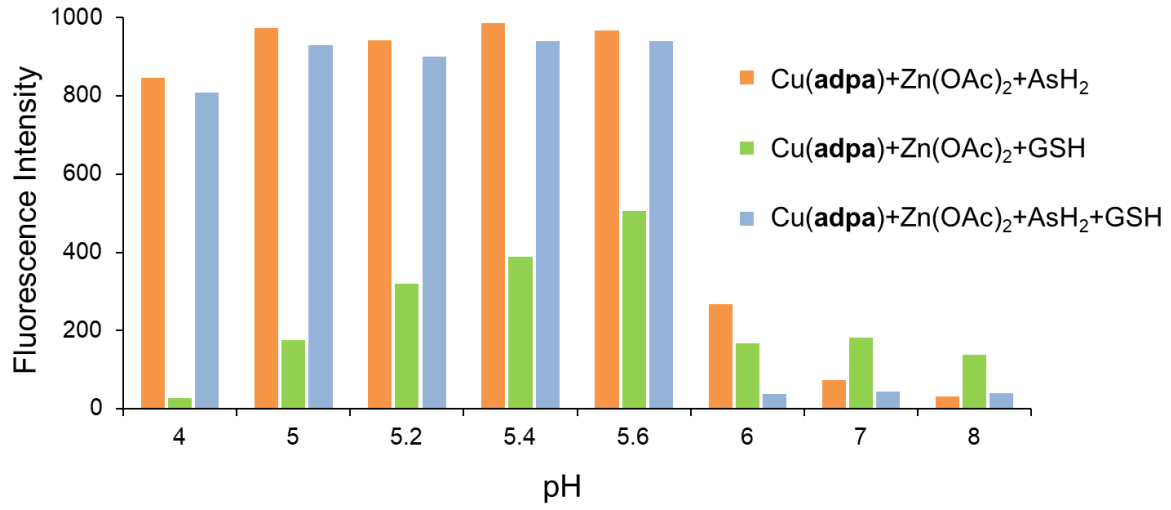


Fig. S19 Fluorescence change of Cu^{II}(**adpa**) + $Zn(OAc)_2$ in the presence of (■) AsH_2, (■) glutathione (GSH) and (■) AsH_2 + GSH at different pH. The pH ranged from 4.0 - 5.6 was controlled by acetic-acetate buffer, whereas that from 6.0 – 8.0 was controlled by phosphate buffer. (Fluorescence parameters: excitation wavelength = 340 nm, slit setting on instrument = 10 and PMT = 500)

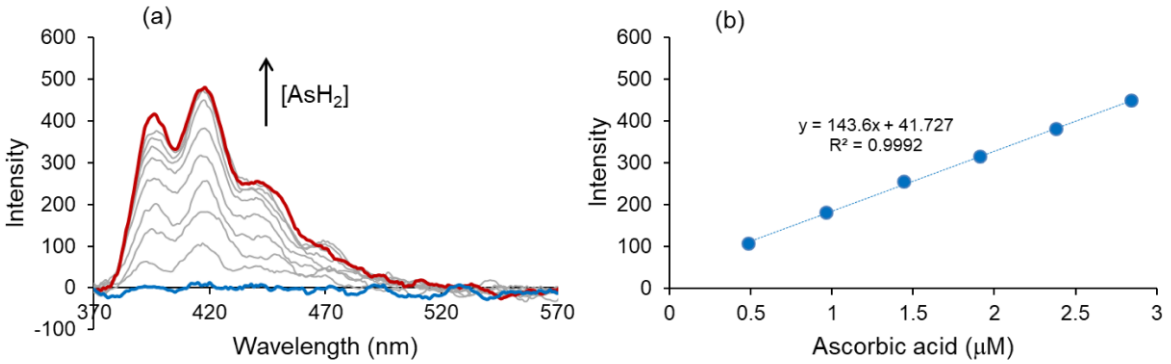


Fig. S20 (a) Fluorescence titration of Cu^{II}(**atpa**) (10 μM) in the presence of $Zn(OAc)_2$ (40 mol equiv.) with AsH_2 (0 – 4.21μM) and (b) plot between fluorescence intensity and concentration of ascorbic acid (μM) (Fluorescence parameters: excitation wavelength = 340 nm, slit setting on instrument = 10 and PMT = 530)

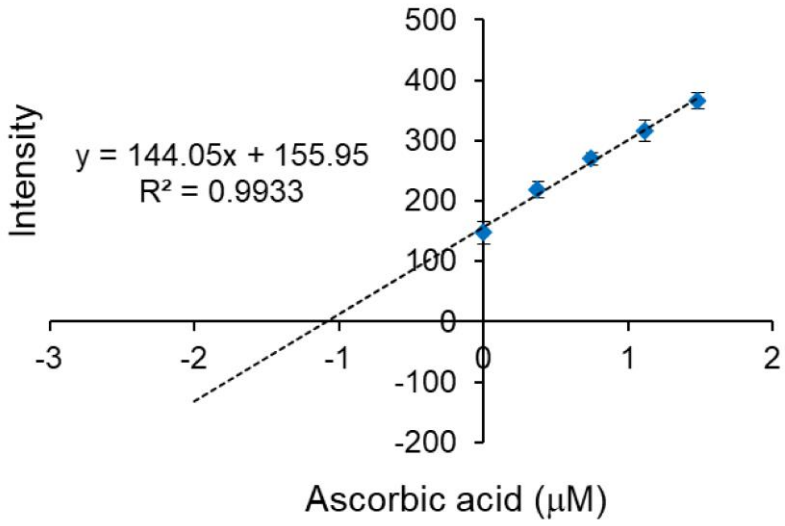
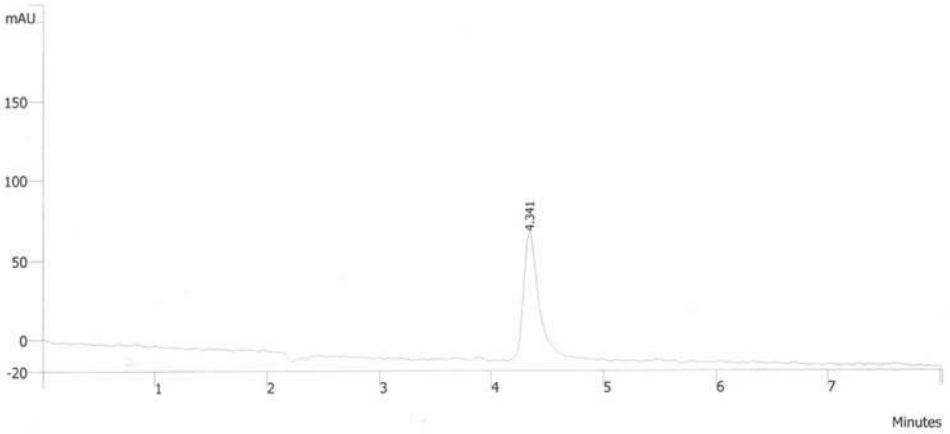


Fig. S21 Standard addition curve for determination of ascorbic acid in vitamin C tablets (Fluorescence parameters: excitation wavelength = 340 nm, slit setting on instrument = 10 and PMT = 530)

Data File:	c:\star\data\31-01-61\20ul vitc	Operator (Calc):	SUNAN
Channel:	1 = 210 nm RESULTS	Calc Date:	01/31/2018 11:19:17
Sample ID:	20ul VitC tablet	Times Calculated:	4
Operator (Inj):	SUNAN	Calculation Method:	20ul vitc tablet10;18;19-1.mth
Injection Date:	01/31/2018 10:18:19	Instrument (Calc):	Varian Star #1
Injection Method:	c:\star\vit c.mth	Run Mode:	Analysis
Run Time (min):	8.023	Peak Measurement:	Peak Area
Workstation:	DISK1	Calculation Type:	Percent
Instrument (Inj):	Varian Star #1	Calibration Level:	N/A
		Verification Tolerance:	N/A



Peak No	Peak Name	Result (%area)	Ret. Time (min)	Area (counts)	Sep. Code
1		100.0000	4.341	7440504	BB
	Totals	**100.0000**		**7440504**	

Status Codes:
U - User defined peak endpoint(s)

Fig. S22 Representative HPLC chromatogram of ascorbic acid analysis in vitamin C tablets

Table S1 HPLC parameters for ascorbic acid detection in vitamin C tablets

HPLC Conditions	
Column	C18, 5 μm, 4.6 × 250 mm, Phenomenex
Mobile Phase	25 mM K-phosphate buffer; pH 2.4
Flow Rate	1.5 mL/min
Oven temperature	30 °C
UV Detection	Wavelength; 210 nm
Injection Volume	20 μL

Table S2 Determination of ascorbic acid in vitamin C tablets by our method using fluorescence spectroscopy

Sample	Taken (μM)	Detected (μM)	Recovery (%)	RSD (%)
Vitamin C tablets	0	1.083	-	-
	0.636	0.652	102.4	3.82
	1.006	1.037	103.1	1.57
	1.372	1.395	101.7	3.90

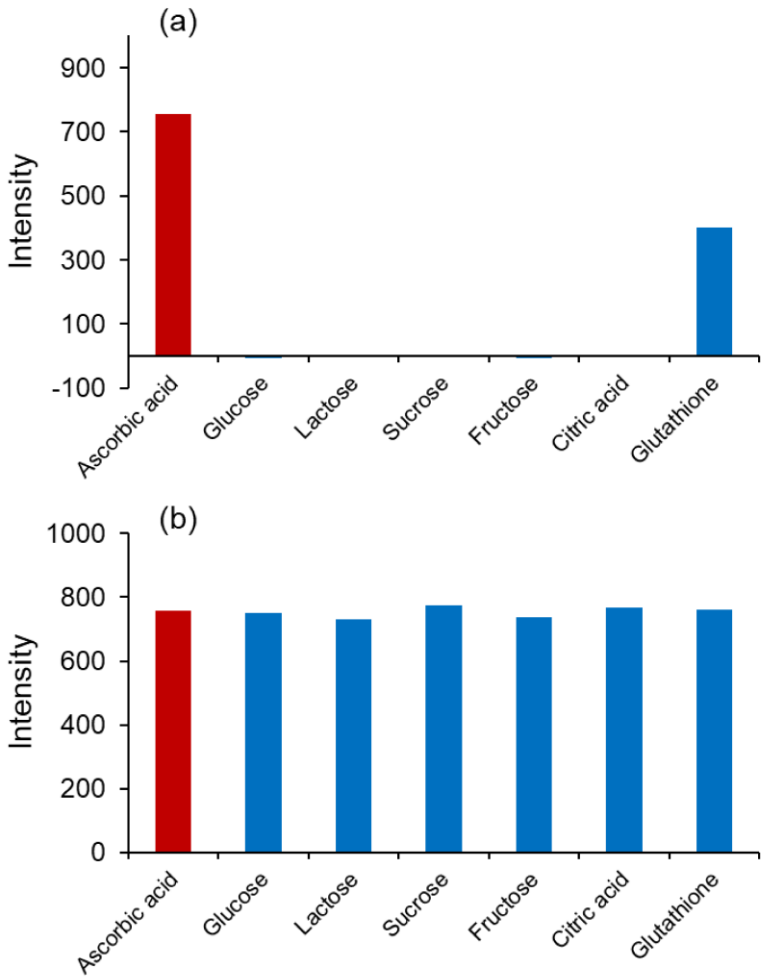


Fig. S23 Fluorescence of Cu^{II}(**adpa**) + $Zn(OAc)_2$ in (a) the absence and (b) the presence of AsH_2 with different natural reducing agents (5.0 mol equiv.); The concentration of Cu(**adpa**) = 10 μM and $Zn(OAc)_2$ = 40 mol equiv. (Fluorescence parameters: excitation wavelength = 340 nm, slit setting on instrument = 10 and PMT = 500)