

Electronic Supporting Information for:

## Reactivity of di(amidoxime) ligand in the presence of Cu(II)/Ni(II)

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Table of contents:

Experimental Details.....	1
NMR Spectra.....	4
Single Crystal X-Ray Diffraction Data and Structure Refinement.....	7
UV Spectra.....	9
Reference.....	12

## Experimental details

### Materials and methods

All chemicals were purchased and used without further purification. Hydroxylamine (50% aqueous solution) and succinonitrile (pur.>99.0%) / glutaronitrile (96.0%) were purchased from Alfa Aesar and TCI respectively. CuCl<sub>2</sub> (98%) was purchased from Shanghai Macklin Biochemical Co., Ltd. NiCl<sub>2</sub> (98%) was purchased from TCI.

Deuterated solvents (D<sub>2</sub>O, TMS, DME-d<sub>7</sub>) were purchased from ACROS Organics, Aladdin, and Innochem, respectively. DCl and NaOD were purchased from Sigma-Aldrich. All <sup>1</sup>H NMR spectra were measured with D<sub>2</sub>O as solvent on a Bruker Magent System 400'54 Ascend spectrometer operating at 400 MHz. And the signals were referred to a TMS external standard.

Single-crystal X-ray diffraction measurements were carried out on a Rigaku Saturn CCD diffractometer at 100(10) K using Cu K $\alpha$  radiation ( $\lambda=1.54184$  Å). An empirical absorption correction was applied using the SADABS program.<sup>1</sup> All structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  using the SHELXL program package.<sup>2</sup> All the hydrogen atoms were geometrically fixed using the riding model.

The absorption spectra from 400 to 200 nm were collected on an Agilent Cary 7000 spectrophotometer with an interval of 0.25 nm and spectral bandwidth of 1.0 nm.

### Synthesis of ligands and complexes

**Ligands:** Glutardiamidoxime (H<sub>2</sub>B) and glutarimidedioxime (H<sub>3</sub>A) were synthesized following the method reported in literatures<sup>3, 4</sup>, recrystallized in aqueous solutions, and then characterized by single-crystal X-ray diffractometry and <sup>1</sup>H NMR.

**Complex 1:** H<sub>3</sub>A (50.61 mg, 0.35 mmol) was dissolved in a 50% H<sub>2</sub>O/ethanol solution (2 mL) in a 5 mL vial. The CuCl<sub>2</sub> (47.44 mg, 0.35 mmol) was added, resulting in a color change from colorless to dark green within seconds. Finally, NaOH (0.35 mL, 0.35 mmol) was added to neutralize the protons of the ligand. The solution was allowed to evaporate at room temperature. Till near dryness, the formed dark green crystallites were filtered, washed with

cold acetone and airdried to get 69.9 mg (79.8%) product. The product was identified to be complex **1** by X-ray diffraction analysis after recrystallization.

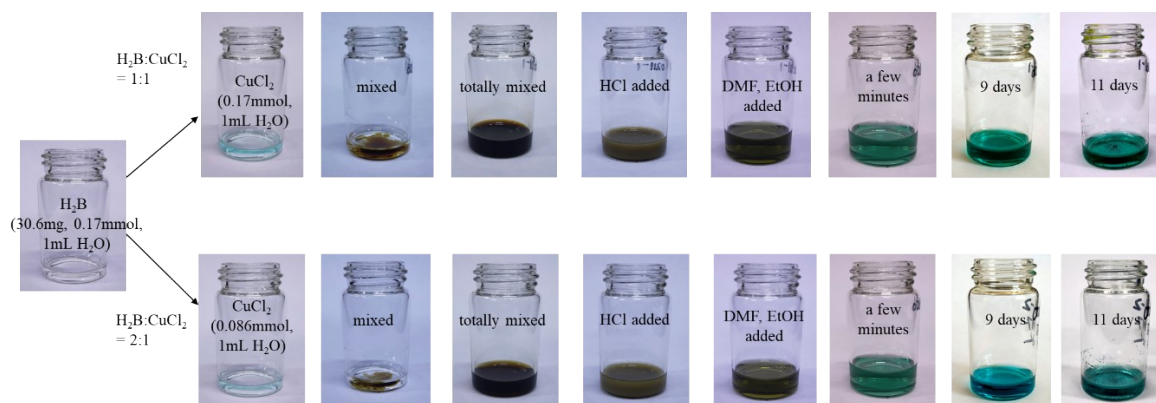
*Growth of single crystals of complex 2:* H<sub>2</sub>B (26 mg, 0.15 mmol) was dissolved in deionized water (1 mL) in a 5 mL vial. Then CuCl<sub>2</sub> solution (0.073 mmol, containing 0.01 mmol HCl) was added, resulting in a color change from colorless to dark green within seconds. Then HCl solution (0.15 mmol) was added and green precipitate formed quickly. After 30 minutes of standing, the supernatant was discarded and DMF/ethanol/water was added until the green precipitate dissolved completely. The resulting green solution was allowed to evaporate slowly at room temperature. After 15 days, some blue green blocks formed and were identified to be complex **2** by single crystal X-ray diffraction analysis.

*Synthesis of complex 2 under basic conditions:* H<sub>2</sub>B (0.50 g, 2.81 mmol) was dissolved in 15 mL deionized water. Then CuCl<sub>2</sub> (0.38 g, 2.80 mmol) was added with magnetic stirring, resulting in a color change from colorless to dark green within seconds. Finally, NaOH solution (2.75 mL, 2.81 mmol) was added to neutralize the protons of the ligand. The solution was allowed to evaporate at room temperature. After 7 days, the formed blue crystallites were filtered, washed with cold acetone and airdried to obtain 0.58 g (91.3%) complex **2**.

*Synthesis of complex 2 under neutral conditions:* H<sub>2</sub>B (0.20 g, 1.13 mmol) and CuCl<sub>2</sub> (0.152 g, 1.13 mmol) were separately dissolved both in 5 mL deionized water in two vials. Then the CuCl<sub>2</sub> solution was added to the H<sub>2</sub>B solution and the color changed from colorless to dark green. Finally, 30 mL of ethanol was added to the mixed solution. The resulting solution was evaporated at room temperature. After 11 days, the formed blue crystallites were filtered, washed with cold acetone and airdried to obtain 0.15 g (58.7%) complex **2**.

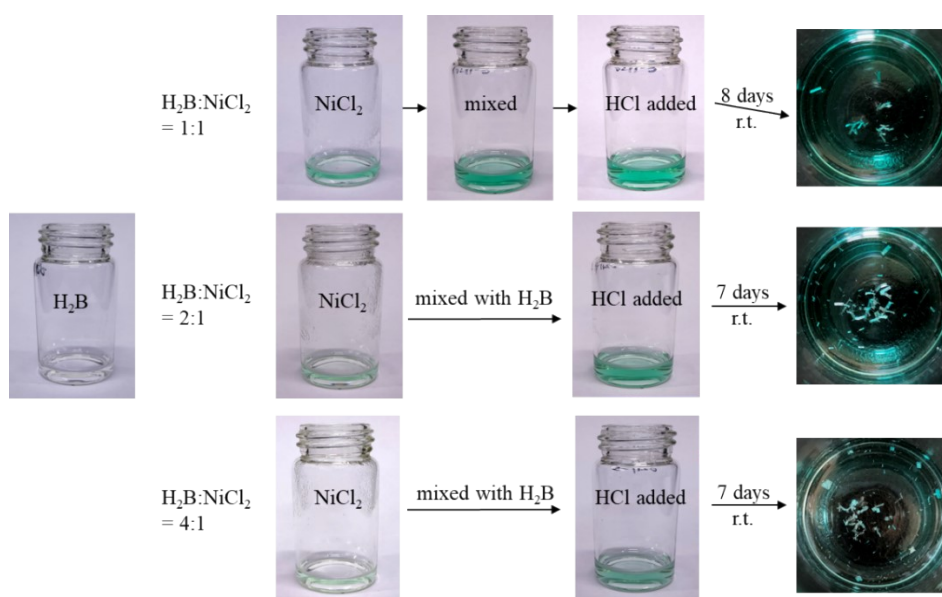
*Synthesis of complex 2 under acidic conditions:* H<sub>2</sub>B (0.30 g, 1.68 mmol) was dissolved in 5 mL deionized water. Then CuCl<sub>2</sub> (0.22 g, 1.65 mmol) was added under magnetic stirring, followed by the addition of HCl solution (1.67 mL, 1.69 mmol). Finally, DMF (6 mL) and ethanol (3 mL) were added to dissolve the resulting solid completely. The solution was allowed to evaporate at room temperature. After 11 days, the formed blue crystallites were filtered, washed with cold acetone and airdried to obtain 0.15 g (39%) complex **2**.

Fig. S1 shows the preparation process of complex **2** under acidic conditions.



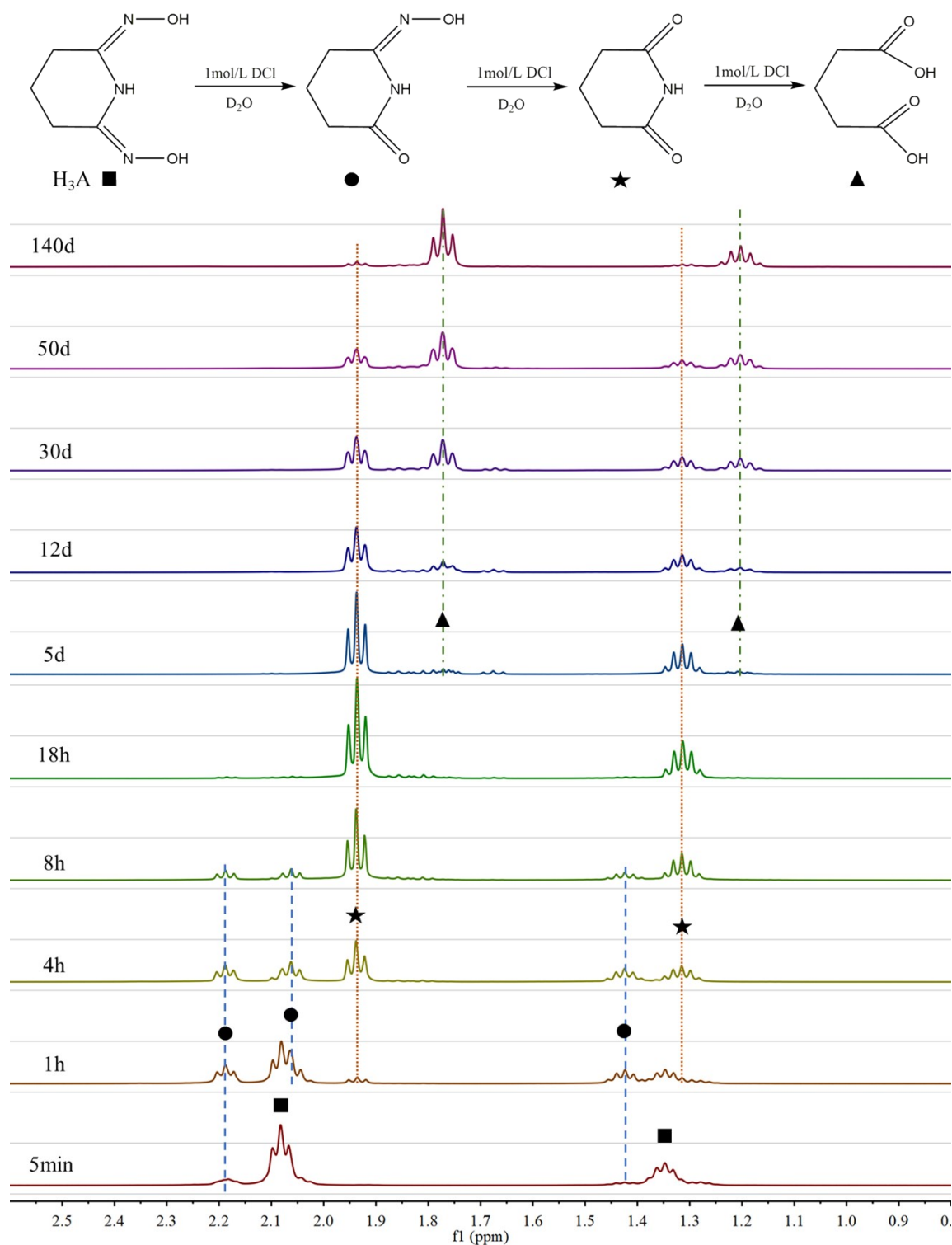
**Fig. S1** The preparation process of complex 2 under acid conditions.

*The synthesis of H<sub>3</sub>A from H<sub>2</sub>B:* Three equal amounts of H<sub>2</sub>B (50.3 mg, 0.28 mmol) were separately dissolved in deionized water (1 mL) in three 10 mL vials. Different amounts of NiCl<sub>2</sub> (36.6 mg/18.4 mg/9.25 mg, 0.28 mmol/0.14 mmol/0.07 mmol) were then added to the vials respectively, resulting in same color changes from colorless to pale green. Finally, 0.28 mmol HCl (aqueous solution) was added to each solution. The solutions were allowed to evaporate at room temperature. One week later, white crystals floating on the surface of the solutions were formed, which were determined to be H<sub>3</sub>A by single crystal X-ray diffraction analysis. Till near dryness, the crystals from each vial were filtered, washed with cold ethanol and airdried to yield 21.5 mg (53%), 24.7 mg (61.1%) and 21.2 mg (52.8%) H<sub>3</sub>A, respectively. The preparation process was shown in Fig. S2.

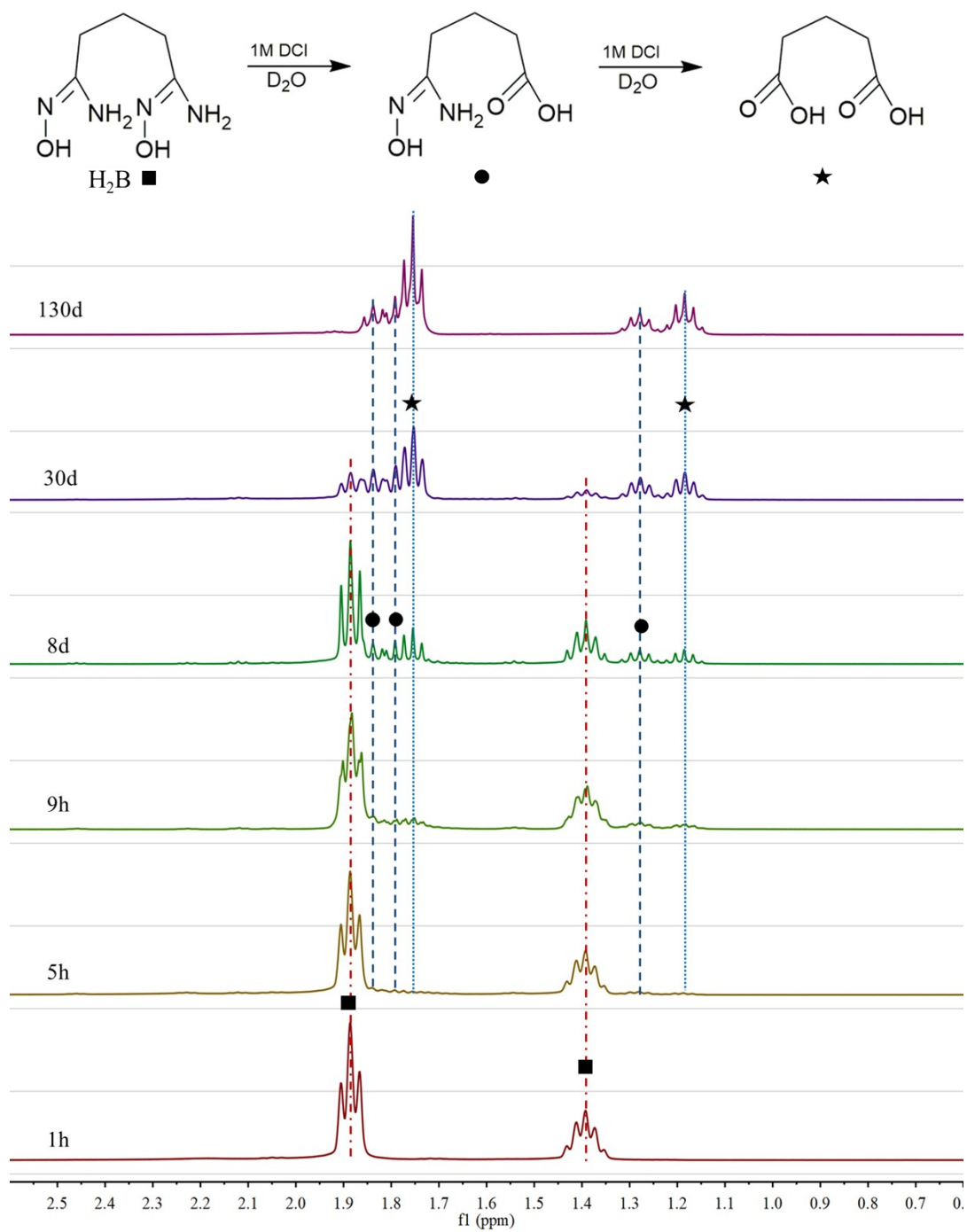


**Fig. S2** The preparation process of H<sub>3</sub>A from H<sub>2</sub>B.

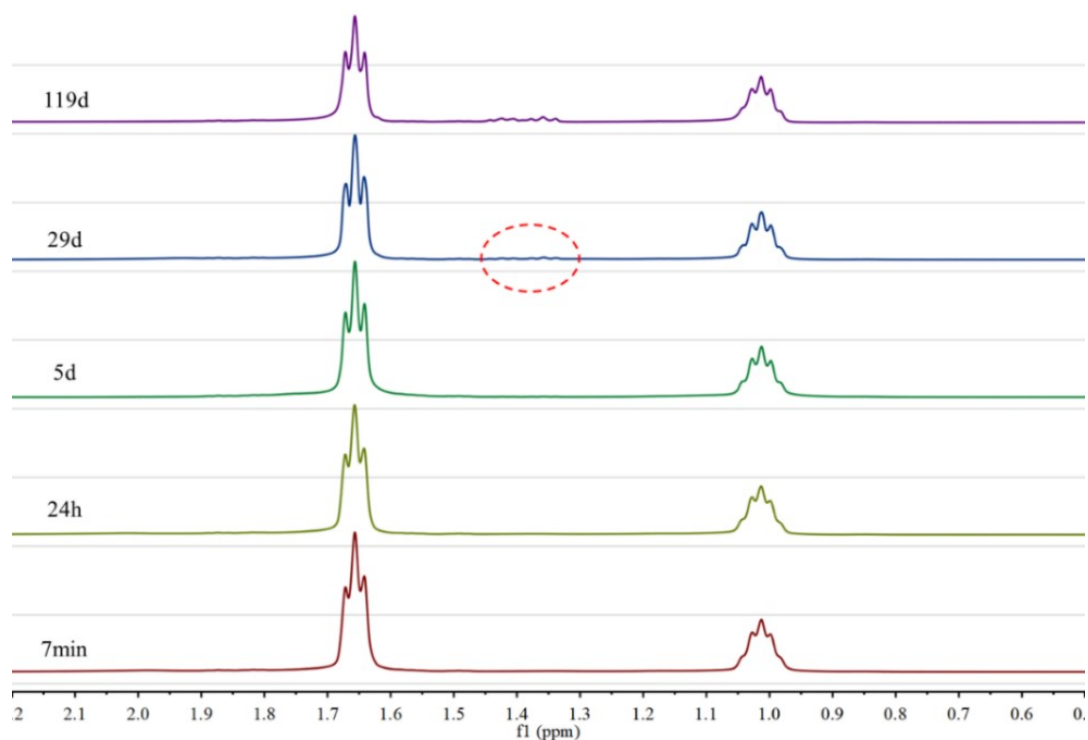
## NMR Spectra



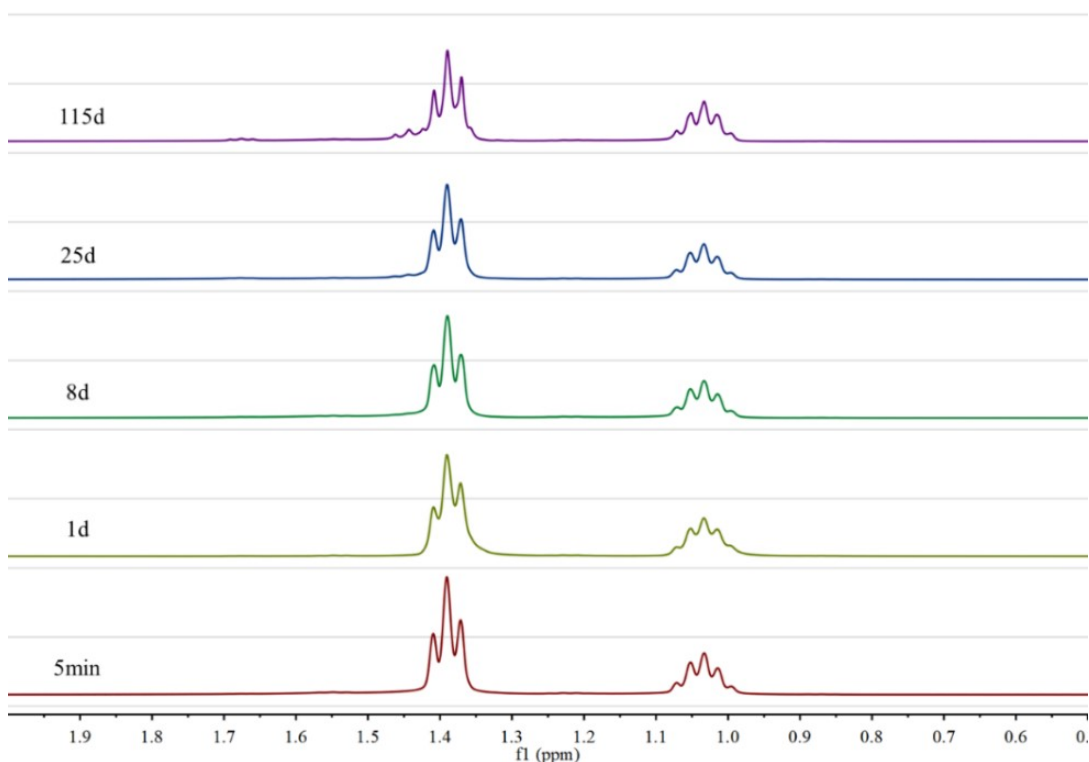
**Fig. S3** Evolution of the  $^1\text{H}$  spectrum of  $\text{H}_3\text{A}$  (0.2 M) over time in 1M DCl at room temperature (400 MHz, solvent  $\text{D}_2\text{O}$ , TMS for external standard  $\delta_{\text{C}}$  0.0 ppm)



**Fig. S4** Evolution of the  $^1H$  spectrum of  $H_2B$  (0.2 M) over time in 1M DCl at room temperature (400 MHz, solvent  $D_2O$ , TMS for external standard  $\delta H$  0.0 ppm).



**Fig. S5** Evolution of the  $^1\text{H}$  spectrum of  $\text{H}_3\text{A}$  (0.2 M) over time in 1M NaOD at room temperature (400 MHz, solvent  $\text{D}_2\text{O}$ , TMS for external standard  $\delta\text{H}$  0.0 ppm).



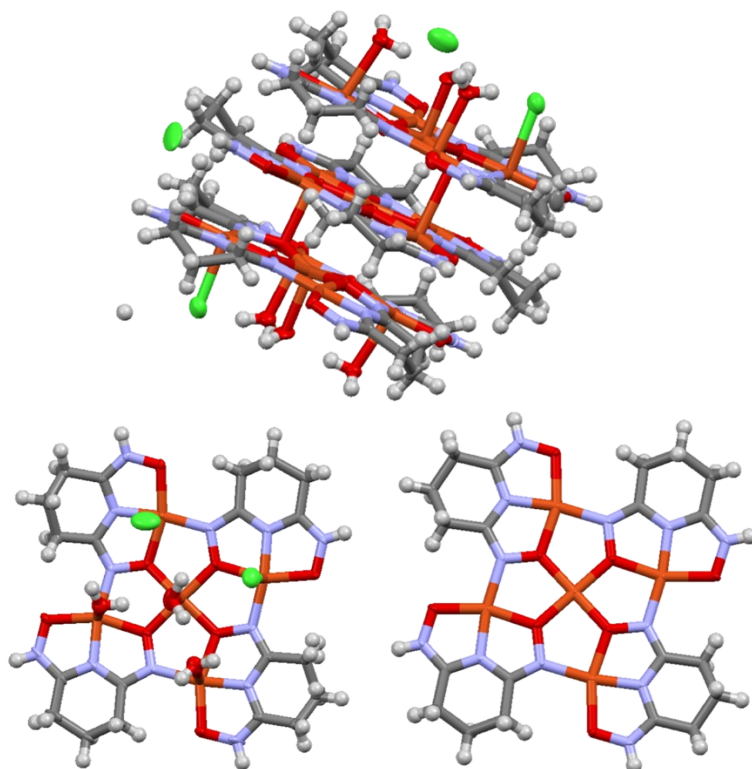
**Fig. S6** Evolution of the  $^1\text{H}$  spectrum of  $\text{H}_2\text{B}$  (0.2 M) over time in 1M NaOD at room temperature (400 MHz, solvent  $\text{D}_2\text{O}$ , TMS for external standard  $\delta\text{H}$  0.0 ppm).

## Single Crystal X-Ray Diffraction Data and Structure Refinement

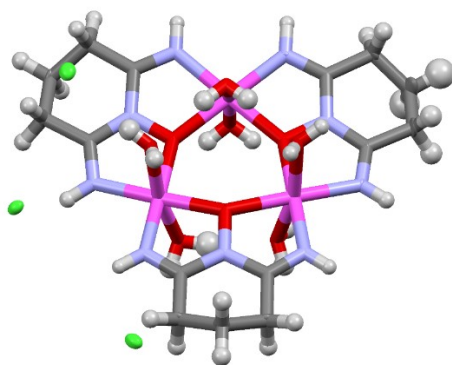
**Table S1.** Crystal data and structure refinement for complexes **1** and **2**.

complex	<b>1</b>	<b>2</b>
Formula	C <sub>60</sub> H <sub>96</sub> Cl <sub>6</sub> Cu <sub>15</sub> N <sub>36</sub> O <sub>30</sub>	C <sub>15</sub> H <sub>24</sub> Cl <sub>3</sub> Cu <sub>3</sub> N <sub>9</sub> O <sub>3</sub>
Formula weight	2967.52	675.40
Temperature	100.00(10) K	100.00(10) K
Crystal system	triclinic	orthorhombic
Space group	P-1	Fdd2
a (Å)	14.2267(10)	13.7421(7)
b (Å)	14.4788(10)	26.2769(12)
c (Å)	16.4283(10)	15.0315(7)
α (deg)	69.591(6)	90
β (deg)	64.511(7)	90
γ (deg)	70.285(6)	90
Volume (Å <sup>3</sup> )	2791.8(4)	5427.9(4)
Z	1	8
D <sub>cal</sub> (g/cm <sup>3</sup> )	1.765	1.653
μ (mm <sup>-1</sup> )	3.016	2.658
F (000)	1485.0	2712.0
Crystal size (mm <sup>3</sup> )	0.2 × 0.2 × 0.2	0.25 × 0.2 × 0.15
2θ range (deg)	6.554 to 59.688	8.036 to 59.62
Reflections collected	31010	5216
R(int)	0.0632	0.0299
Data/restraints/parameters	13382/ 6/ 675	2729/ 31/ 157
Goodness-of-fit on F <sup>2</sup>	1.036	1.089
R <sub>1</sub> [I>2σ(I)]	R <sub>1</sub> = 0.0561	R <sub>1</sub> = 0.0492
wR <sub>2</sub> (all data)	wR <sub>2</sub> = 0.1481	wR <sub>2</sub> = 0.1314
Largest peak/ hole (e.Å <sup>-3</sup> )	2.09/ -1.81	1.32/ -1.32





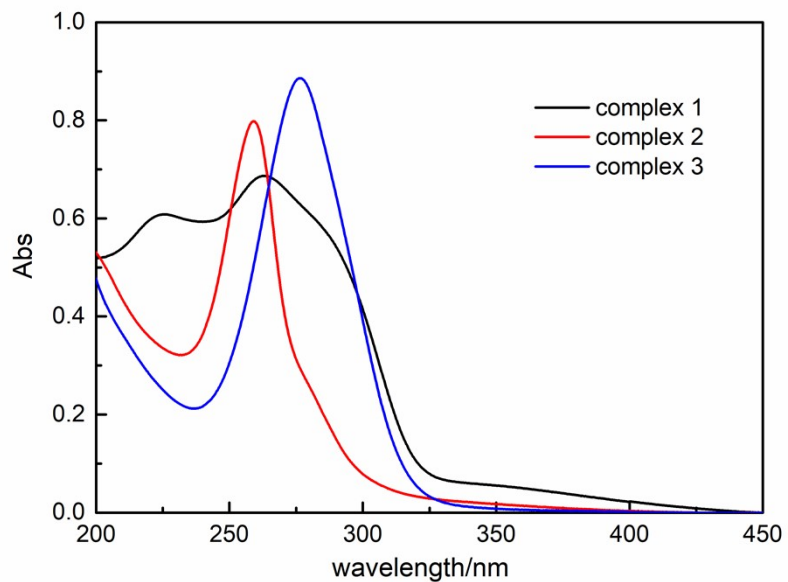
**Fig. S7** Full crystal structure of complex **1** (top) and crystal formula unit (bottom) shown as ellipsoids at 50% probability. Orange = Cu, Green = Cl, red = O, purple = N, gray = C, white = H.



**Fig. S8** Full crystal structure of complex **3** shown as ellipsoids at 50% probability. Pink = Ni, Green = Cl, red = O, purple = N, gray = C, white = H.

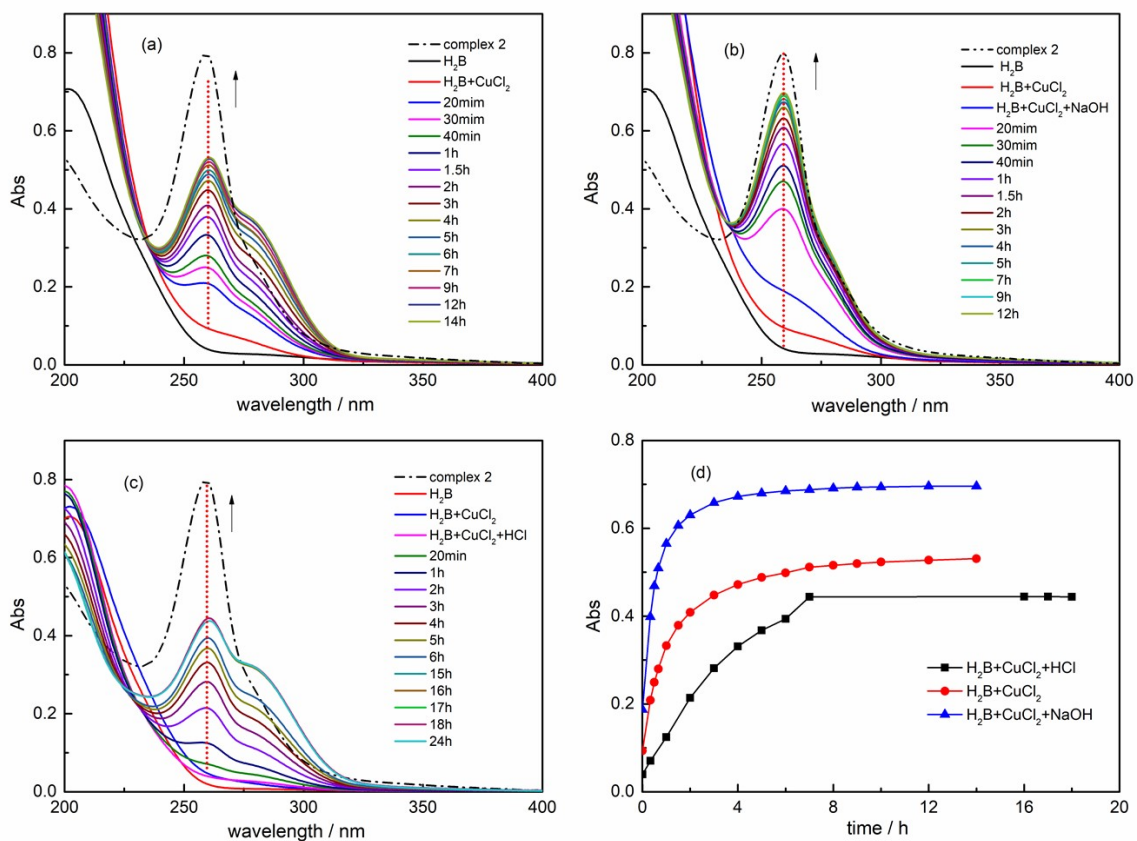
## UV-Visible absorption spectra

The absorption spectra of three complexes dissolved in deionized water are shown in Fig. S9., where the absorption spectra of complexes **2** and **3** are the same as those given in the literature.<sup>5</sup>



**Fig. S9** Absorption Spectra of the complexes **1** ( $[\text{Cu}_5(\text{HA})_4(\text{H}_2\text{O})\text{Cl}]_2[\text{Cu}_5(\text{HA})_4](\text{Cl})_4(\text{H}_2\text{O})_4$ ), **2** ( $\text{Cu}_3(\text{H}_2\text{A}')_3\text{Cl}_3$ ) and **3** ( $[\text{Ni}_3(\text{H}_2\text{A}')_3(\text{H}_2\text{O})_6]\text{Cl}_3$ ) solutions.

The reaction of  $H_2B$  with  $Cu(II)$  under different pH conditions were further monitored by absorption spectroscopy. As shown in Fig. S10, complex **2** could be formed under neutral/alkaline/acidic conditions. But only in alkaline condition no byproduct was found and the reaction rate was obviously faster than those in the other two conditions.



**Fig. S10** Variations in the absorption spectra of mixed solutions of  $H_2B$  and  $CuCl_2$  under different pH conditions: (a) 0.05 mM  $H_2B$ , 0.05 mM  $CuCl_2$ ; (b) 0.05 mM  $H_2B$ , 0.05 mM  $CuCl_2$ , 0.05 mM  $NaOH$ ; (c) 0.05 mM  $H_2B$ , 0.05 mM  $CuCl_2$ , 0.05 mM  $HCl$ ; (d) the intensities at 260 nm of the spectra in (a), (b), and (c).

## Reference

1. G. M. Sheldrick, *Sadabs*, 1996.
2. G. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112-122.
3. G. Tian, S. J. Teat, Z. Zhang and L. Rao, *Dalton Trans*, 2012, **41**, 11579-11586.
4. G. Tian, S. J. Teat and L. Rao, *Dalton Trans*, 2013, **42**, 5690-5696.
5. Z. C. Kennedy, A. J. P. Cardenas, J. F. Corbey and M. G. Warner, *Chemical Communications*, 2016, **52**.