Supplementary Information

A study on one-step laser nanopatterning onto copper-hydrazone-complex thin films and its mechanism

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1 Synthesis of the hydrazone ligand (HL)

The hydrazone ligand (HL) was synthesized using a diazo component (3-Amino-5-methylisoxazole) and a coupling component (1, 3-dimethlybarbituric acid) according to the published methods [1-3]. Typically, 3-amino-5-methylisoxazole (2.00 g, 0.020 mol) was dissolved in 40 mL concentrated phosphoric acid (85%) at room temperature. The solution was then cooled to -5–0 ºC in an ice-salt bath and maintained at this temperature while a solution of sodium nitrite (1.52 g, 0.022 mol) in water (10 mL) was then added dropwise within 1 h under continuous stirring, and the ensuing mixture was stirred at 0–5 ºC for a further 1 h. The resulting diazonium solution was then used directly for the next step. The 1,3-dimethlybarbituric acid

(3.44 g, 0.022 mol) was dissolved in sodium hydroxide solution (150 mL, 2.5%) and cooled to -5–0 ºC in an ice-salt bath. The above diazonium solution was added to the stirred coupling component solution at -5–0 ºC for 30 minutes. The mixture was allowed to rise to room temperature over 4 hours and the pH value was lowered to about 5. The precipitated solid was collected by filtration, washed with water, and then vacuum dried. The rough product was finally recrystallized from ethanol/ water mixtures (3:1) to form white crystals. Yield: 5.30 g (90.0%). M.p. 193-195 ºC. Anal. Calcd (found) for $C_{10}H_{11}N_5O_4$: C, 45.28 (45.25); H, 4.18 (4.14); N, 26.41 (26.38). ^{1}H NMR ($CDCl_3$, TMS, δ ppm): 2.457(s, 3H, CH_3), 3.389(s, 3H, CH_3), 3.421(s, 3H, CH_3), 6.497(s, 1H, isoxazole-H), 14.328 (s, br, 1H, hydrazone NH). UV-Vis spectra in chloroform: λ_{max} (nm)(logε)= 352(4.39). FT-IR spectra (KBr pellets, cm^{-1}): 3155(*vH-N*, hydrazone), 1732(*vC=O*), 1676(*vC=O*), 1649(*vC=O···H*), 1608(*vCH=N*, isoxazole), 1512(*vN-N=C*, azo methine), 922(*vN-H···O*). EI-MS Found(Calcd): m/z= 265(265)[M^+].

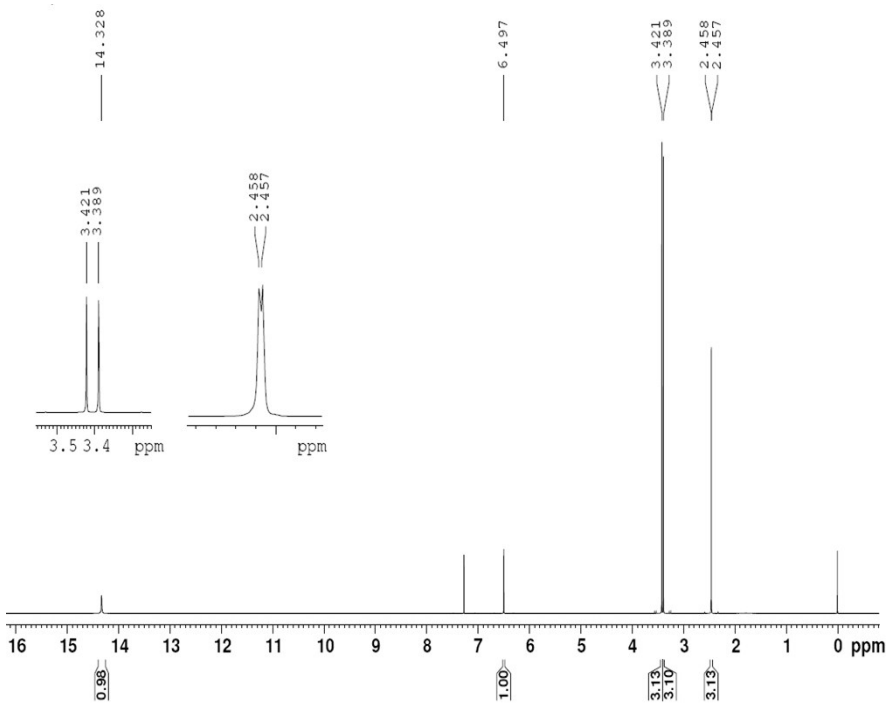

Fig. S1 ^{1}H-NMR of the *HL*.

2 Synthesis of the CuL_2 complex

The CuL_2 was prepared by the same general method: the resulting hydrazone ligand

(HL) (0.50 g, 1.81 mmol) was dissolved in absolute methanol solution (20 mL) at room temperature and the copper(II) acetate (0.18 g, 1.00 mmol) in powders was added under vigorous stirring. The ensuing mixture was stirred under reflux for further 4–5 h. After cooling, the precipitated solid was collected by filtration, washed with water and then vacuum dried. The acquired products were characterized and used directly without further purification. Brown powder. Yield: 96.1%. M.p. > 230 ºC (dec.). Anal. Calcd (found) for $C_{20}H_{20}N_{10}O_8Cu$: C, 40.58 (40.69); H, 3.41 (3.53); N, 23.66 (23.74); Cu, 10.73 (10.61). UV-Vis spectra in chloroform: λ_{max} (nm)(logε)= 378(4.53). MALDI-MS Calcd (Found): *m/z*= 591.08 (592.0834) [M+H$^+$].

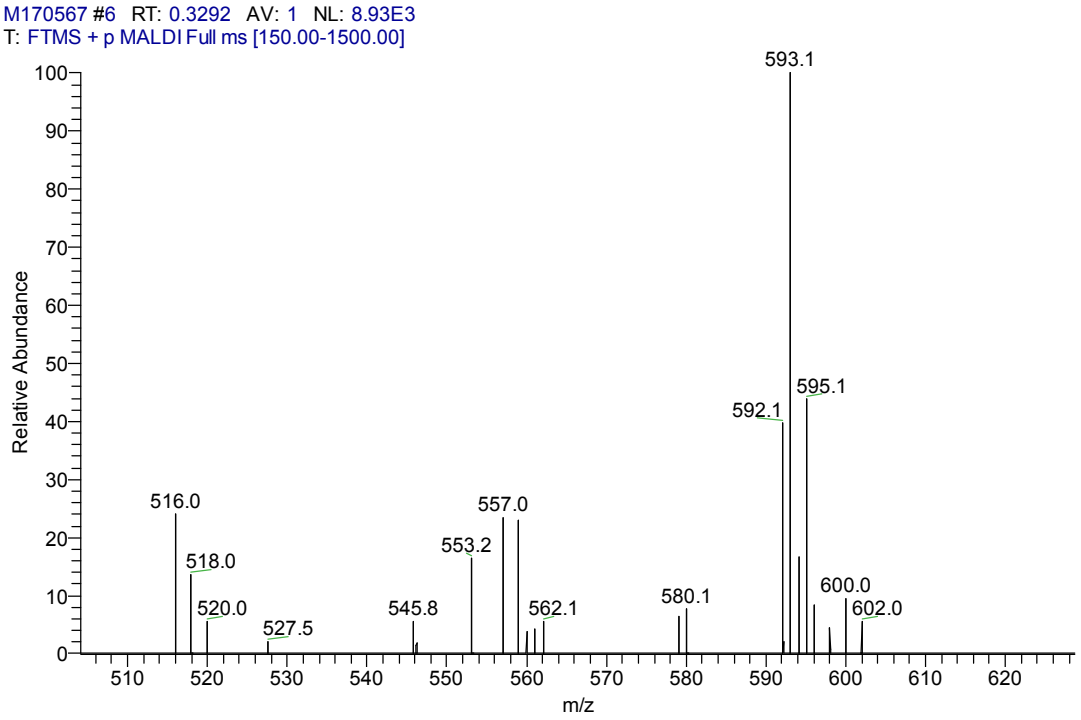

Fig. S2 MALDI-MS of *CuL_2 complex*

[1] Z. Chen, Y. Wu, C. He, B. Wang, D. Gu and F. Gan, *Synth. Metal*, 2010, **160**, 2581.

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[3] Z. Chen, Y. Wu, D. Gu and F. Gan, *Dyes and Pigments*, 2010, **86**, 42.