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Supporting Information

for

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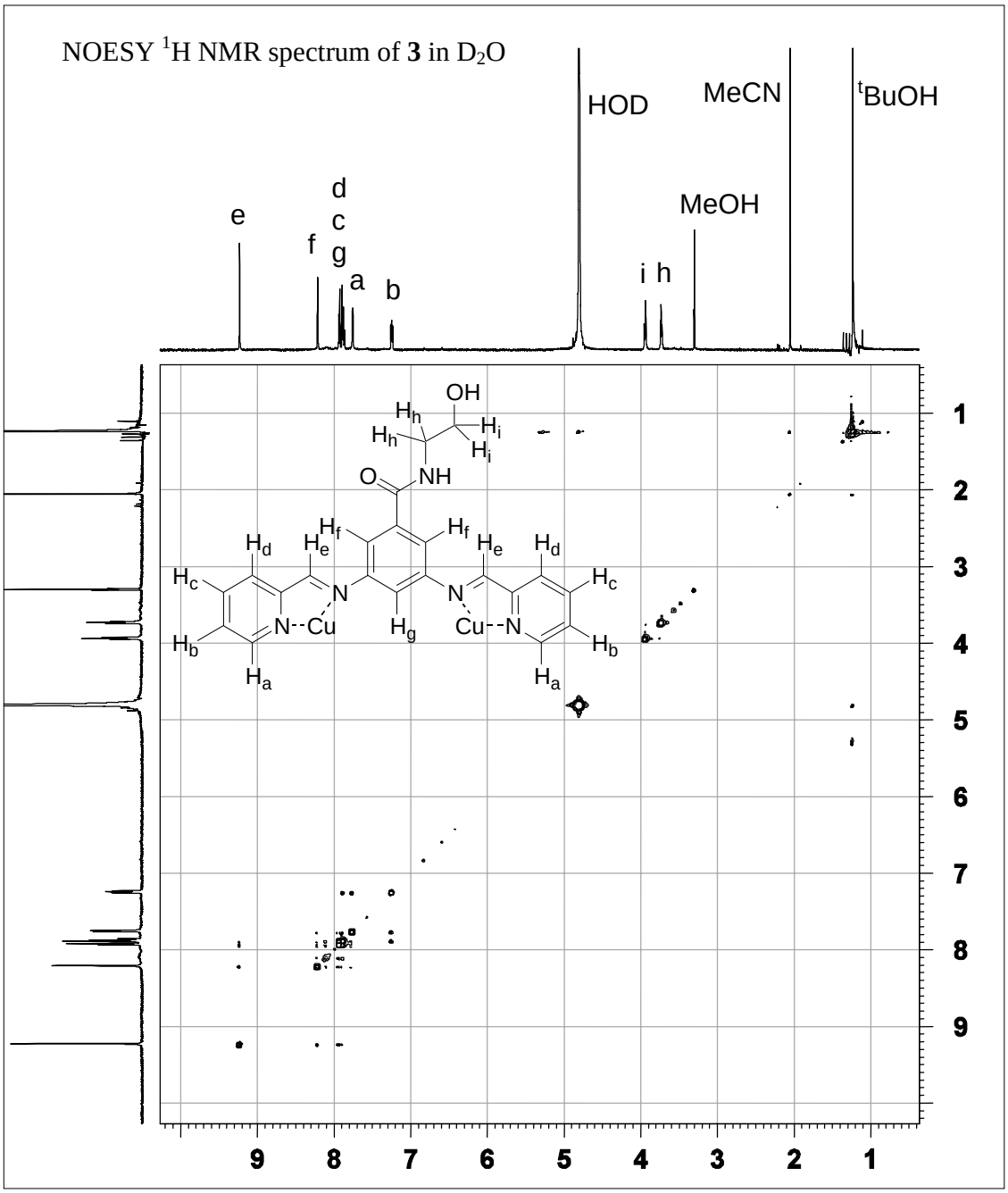
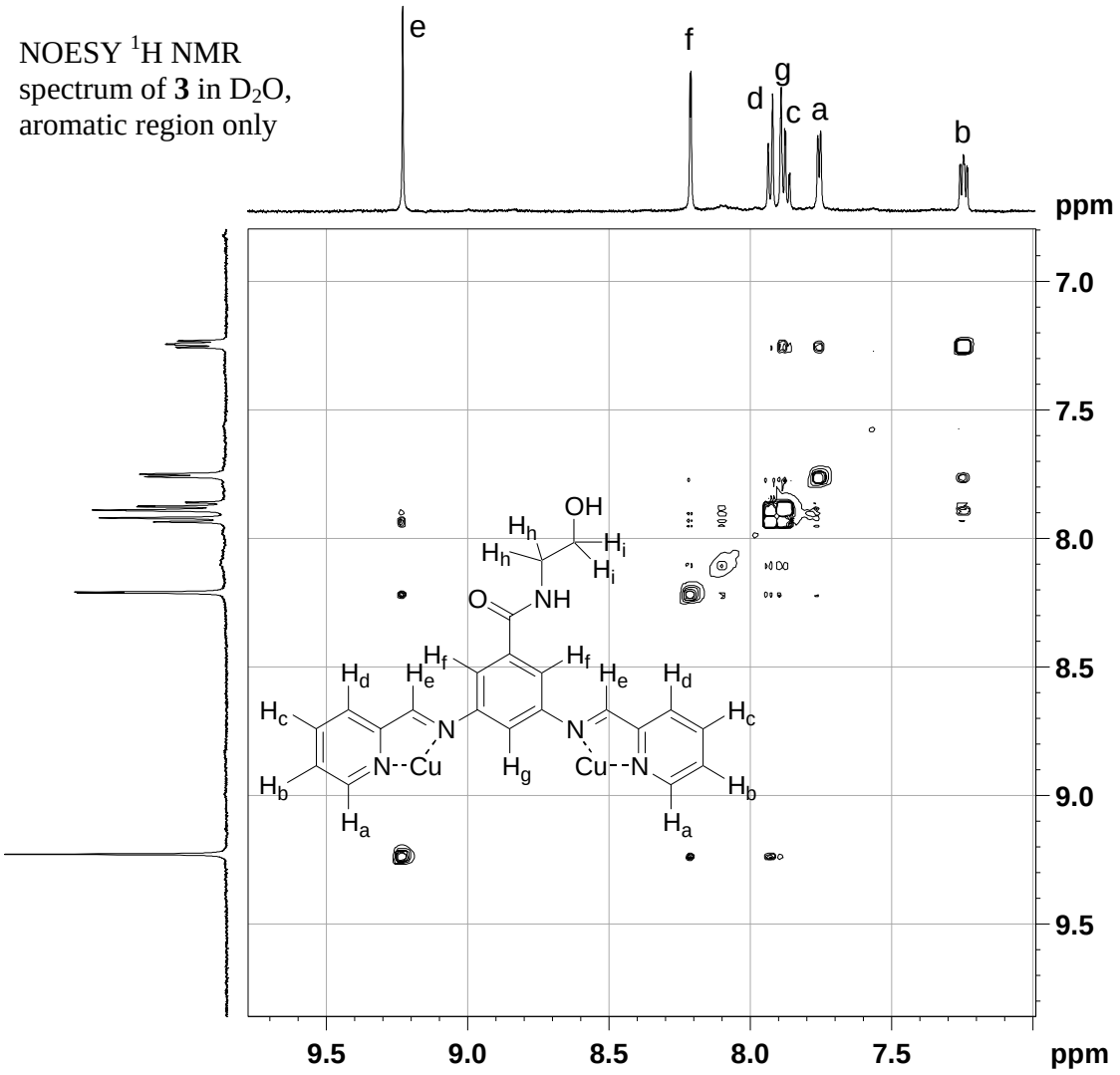
Supporting information for "Hydrophobic Effect as a Driving Force in the Self-Assembly of a [2 × 2] Copper(I) Grid" by Jonathan R. Nitschke,* Marie Hutin, and Gérald Bernardinelli





Synthesis of 3,5-diamino-N-(2-hydroxy-ethyl)-benzamide (1): Into a 10 ml Schlenk flask was loaded methyl-3,5-diaminobenzoate (1.26 g, 7.62 mmol) and 2-aminoethanol (5.05 g, 82.7 mmol). The atmosphere was purified of dioxygen by three evacuation / argon-purge cycles, and the mixture was stirred until the solids dissolved. The light orange solution was then placed in an oil bath at 373 K and stirred at this temperature for 3 h. The mixture was then allowed to cool to room temperature, and volatiles were removed under dynamic vacuum during 12 h. The product was recrystallised from a mixture of water and 2-methyl-2-propanol, and obtained as white microcrystals. The isolated yield was 1.19 g, 80 %. ^{1}H NMR (400 MHz, 300 K, D_2O, referenced to 2-methyl-2-propanol at 1.24 ppm as internal standard): δ = 6.59 (d, J = 2.0 Hz, 2H, 2,6-phenylamide), 6.42 (t, J = 2.0 Hz, 1H, 4-phenylamide), 3.73 (t, J = 5.5 Hz, 2H, ethanolamide), 3.47 (t, J = 5.5 Hz, 2H, ethanolamide); ^{13}C NMR (100.62 MHz, 300 K, D_2O, referenced to the methyl groups of 2-methyl-2-propanol at 30.29 ppm as internal standard): δ = 171.2, 147.6, 135.8, 106.7, 105.9, 59.92, 41.85.; EI-MS *m/z* = 195 (**1**$^+$), 177 (**1**$^+$ - H_2O) 135 (**1**$^+$ - $NHCH_2CH_2OH$); Anal. Calcd for $C_9H_{13}N_3O_2$: C 55.37, H 6.71, N 21.52; Found C 55.19, H 6.76, N 21.40.

Attempts at the synthesis of 3 in different solvents: Diamine **1** (0.02 mmol) was mixed with pyridine-2-carboxaldehyde **2** (2 equiv) and copper(I) tetrakis(acetonitrile)tetrafluoroborate (1 equiv) in the solvent noted below (0.7 ml) under an argon atmosphere.

Deuterated solvent	Solution color	Solubility	Appearance of the NMR spectrum
DMSO-d_6	purple-orange	poor	broad peaks
CD_3OD	purple	poor	broad peaks
CD_3CN	yellow-orange	poor	numerous peaks
CD_3NO_2	pink-orange	poor	broad peaks
$CDCl_3$	orange	poor	pyridinecarboxaldeyde and CH_3CN observed
C_6D_6	light yellow	poor	pyridinecarboxaldeyde observed
Acetone-d_6	red-pink	poor	broad peaks

Non-deuterated solvent	Solution color	Solubility	Analytical technique
DMF	purple-orange	good	ES-MS : showed only the formation of $[CuL]^+$ (m/z=436.3)
Pyridine	light orange	good	None
Et_2O	colorless	very poor	None
CH_3COOH	purple	poor	NMR : numerous peaks
THF	yellow-orange	poor	None

Solubility good: all products were soluble
Solubility poor: insoluble products were observed