Unusual Oxidation of an N-heterocycle Ligand in Metal-organic Framework

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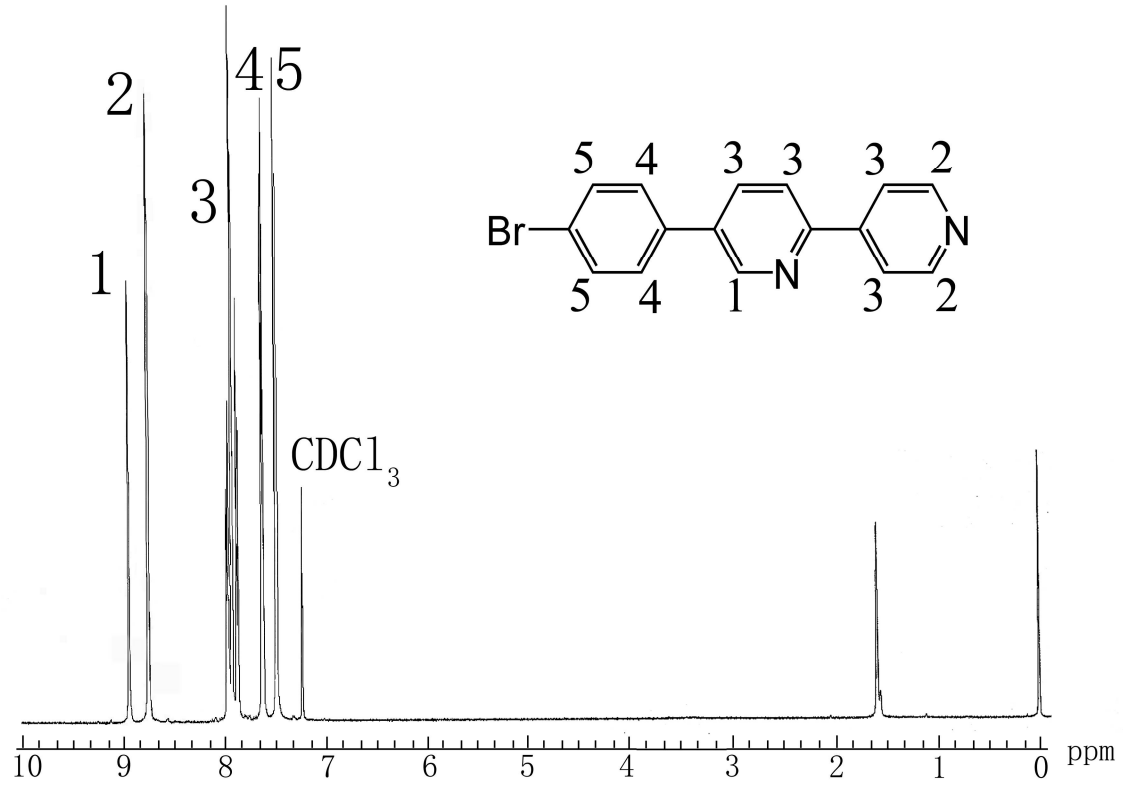
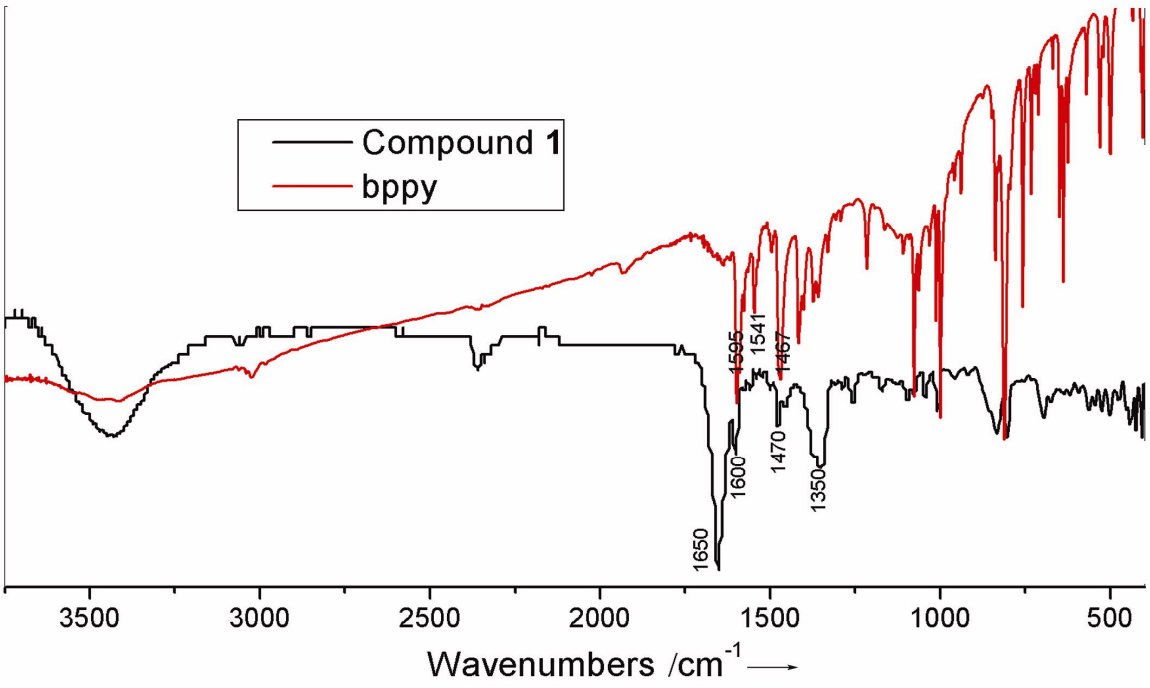
Supporting Materials:

A mixture solution of $Cu(NO_3)_2$(248.7 mg, 1.0 mmol), Na_2MoO_4(488.9 mg, 2.1 mmol) and bppy(124.0 mg, 0.4 mmol) was adjusted to *ca.* pH 4.60 with dilute H_3PO_4 solution. The resultant mixture was sealed in a 25 mL Teflon-lined autoclave (70% full) and heated at 170 °C for 96h. The autoclave was then cooled at 10 °C per hour to RT. Blue crystals of **1** were obtained (yield: 79.1 mg, 63% based on bppy) along with a few yellow crystals which was characterized as salts of Keggin type polyoxometalate (see S-Fig. 3). The blue crystals were washed with water and dried in a desiccator at ambient temperature. Elemental analysis(%) calcd for $C_{24}H_{14}Br_2Cu_1N_2O_4$: C 46.66, H 2.28, N 4.53; found: C 46.32, H 2.37, N 4.26. IR(cm^{-1})(see S-Fig. 2): ν = 1650(s), 1600(m), 1480(m), 1350(m), 1260(w), 1170(w), 1040(w), 1010(w), 833(m), 804(m), 694(w), 501(w) and 444(w).

S-Fig. 1 A room temperature ^{1}H NMR spectrum of bppy in $CDCl_3$, tetramethylsilane (TMS) was used as an internal reference.



S-Fig. 2 IR spectra of bppy and compound **1**.



S-Fig. 3 IR spectrum of Keggin type polyoxometalate.