Supporting Information

Sorption-desorption behavior of bispyrazolato-copper(II) 1D- polymers.

by

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Syntheses.

[Cu(μ-pz)$_2$·H$_2$O], 1.

Method A) A solution of 2.00 g of Cu(MeCOO)$_2$·H$_2$O (10.02 mmol) in 200 mL of MeCN was treated at r.t. with 1.40 g of Hpz (20.56 mmol) dissolved in 10 ml of MeCN. The solution immediately turned deep blue and after a few seconds a light-blue solid formed, which turned into a pale pink solid by stirring for 2 or 3 minutes. The suspension was further stirred for 30 minutes, the solid filtered, washed with 3 portions of 20 mL of MeCN and dried in air. Yield 2.12 g (98%). Acetic acid was found in the colorless mother liquors.

1: mp. 304-305 °C (dec). Elem. Anal. Calcd for $C_6H_8N_4OCu$: C, 33.41; H, 3.74; N, 25.97. Found: C, 33.86; H, 3.81; N, 25.70. IR (nujol, cm^{-1}): 3617, 3546, 1614, 1276, 1178, 1064, 1054, 888, 785, 761, 677, 640, 632, 364, 333, 285, 268; μ_{eff} (296 K): 1.498 BM.

Method B)

Copper(II) propionate (0.96 g, 4.6 mmol) was dissolved in 30 mL of MeCN and a solution of Hpz (0.96 g, 14.2 mmol) in 40 mL of MeCN was added under stirring. A pink precipitate immediately formed. The suspension was stirred for 2 h and let to stay overnight, yielding a pink powder that was filtered, washed with 5 mL of MeCN. Yield 0.99 g, 98 %. Compound **1** was also obtained by using other copper carboxylates, actually, formate, propionate, butyrate and valerate and carrying out the reaction according to the procedure above reported.

Anal. Calcd for $C_6H_8N_4OCu$: C, 33.41; H, 3.74; N, 25.97. Found: C, 33.68; H, 3.84; N, 25.83.

[β-Cu(μ-pz)$_2$], 3.

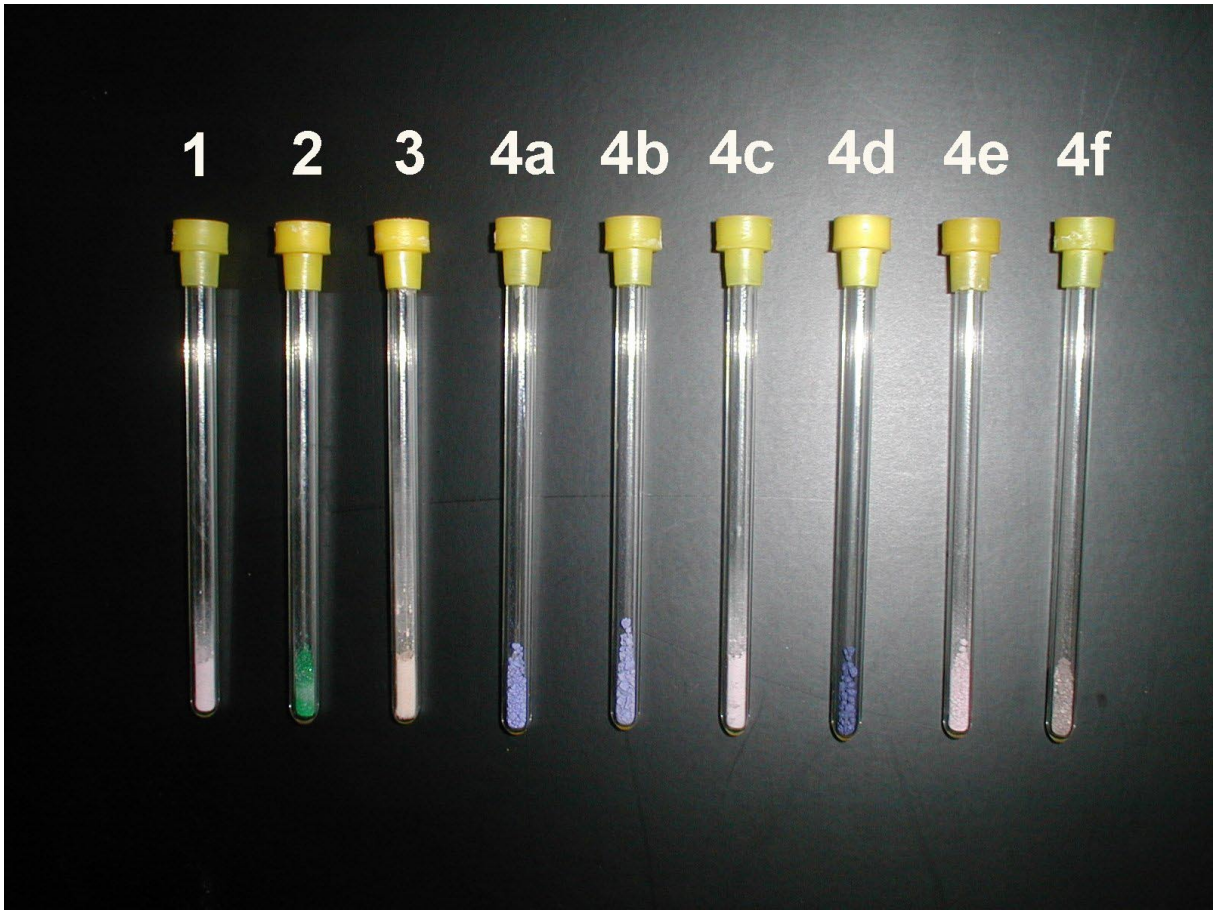
Solid compound **1** was dried by pumping it at 0.1 mm Hg and *ca.* 100 °C for 1 h (alternatively at 130 °C without pumping), obtaining a beige solid, which was identified as **3**.

3: mp. 302-303 °C (dec). Elem. Anal. Calcd for $C_6H_6N_4Cu$: C, 36.45; H, 3.06; N, 28.34. Found: extremely hygroscopic, analysis n.a. (see Table 1 and text)

Interaction of 3 with Lewis bases. Synthesis of compounds 1 and 4a-f

Compound **3** interacts at r.t. with several gaseous substances, giving differently colored compounds (see Figure S1), according to the following general procedure.

Figure S1: numbering as in Table 1 of the pertinent paper:



About 200 mg of **3** were weighed into an open vial which was then put into a 25 mL Schlenk tube. The tube was then evacuated and a small amount of the reagent was introduced through a serum cap (liquids) or a faucet (gases). The sorption was favored by gently shaking the vial for periods varying from a few minutes to days, depending on the reagent. Results are summarized in Table 1.

Compound **4c** was also obtained by reacting anhydrous $Cu(MeCOO)_2$ with Hpz in anhydrous MeCN.

Selected Uv-Vis absorption data

Table S1: $\lambda_{(max)}$ from solid state reflectance electronic spectra of compounds **1**-**4**

Compound	$\lambda_{(max)}$, (nm)
1	317, 361, 501, 589 (shoulder)
2	333, 442 (shoulder), 563 (shoulder), 610, 653
3	320, 385 (shoulder), 496, 588 (shoulder)
4a	321, 360 (shoulder), 561, 642 (shoulder)
4b	323, 359 (shoulder), 566, 640 (shoulder)
4c	315, 364, 502, 592 (shoulder)
4d	325, 368 (shoulder), 560, 640 (shoulder),
4e	314, 360 (shoulder), 501, 592 (shoulder)
4f	324, 361 (shoulder), 500, 590 (shoulder)

Selected IR absorption data

Compound **1**: $[Cu(pz)_2].H_2O$: 3617m, 3546m (OH), 3126w, 3106w (CH), 1614m (OH), 1485 m (C-C), 888m, 785s, 761s, 677w, 640, 632m, 364m, 333s, 285m, 268m.
Compound **3**, β-$[Cu(pz)_2]$: 3117w (CH), 1573w, 1485m (C-C), 879, 781m, 745m, 674w, 627m, 358m, 334s, 269m, 246w, 239w.
Compound **4a**: $[Cu(pz)_2].NH_3$: 3372br, 3281 (NH), 3124w, 3104w (CH), 1556br (C-C), 1485m, 885m, 784s, 759s, 679w, 640m, 632m, 433br, 383br, 324s, 304sh, 267w.
Compound **4b**: $[Cu(pz)_2].MeNH_2$: 3200br (NH), 3124w, 3104w (CH), 1556br (C-C), 1485m, 885m, 784s, 759s, 679w, 640m, 632m, 433br, 383br, 324s, 304sh, 267w.
Compound **4c**: $[Cu(pz)_2]$.MeCN: 3111w (CH), 2248m (CN), 1483m, 878m, 771s, 752s, 678w, 632m, 389w, 348m, 332s, 268m, 237w.
Compound **4d**: $[Cu(pz)_2]$.py: 3130w, 3104w (CH), 1592m, 1573w, 1485m, 876w, 846w, 677w, 640, 633m, 628m, 614w, 415w, 362br, 333s, 322m, 304m, 280m, 269m, 232w.
Compound **4e**: [Cu(pz)].EtOH: 3189w, 3124w, 3104w, 1600w, 1485m, 889m, 785s, 759s, 677m, 640m, 632m, 366br, 333m, 280br, 268m.
Compound **4f**: [Cu(pz)].MeOH: 3189w, 3130w, 3104w, 1600w, 1560w, 1485m, 889m, 785s, 761s, 677m, 640m, 632m, 366br, 333m, 305br, 292br, 280br, 268m, 250w.

R.t. Magnetic susceptibility data

Compound **1**: $[Cu(pz)_2].H_2O$: 1.52 BM
Compound **3:** β-$[Cu(pz)_2]$: 1.50 BM
Compound **4a**: $[Cu(pz)_2].NH_3$: 1.53 BM
Compound **4b**: $[Cu(pz)_2].MeNH_2$: 1.53 BM
Compound **4c**: $[Cu(pz)_2]$.MeCN: 1.46 BM
Compound **4d**: $[Cu(pz)_2]$.py: 1.55 BM
Compound **4e**: [Cu(pz)].EtOH: 1.48 BM
Compound **4f**: [Cu(pz)].MeOH: 1.50 BM