Supporting Information for:

Control of molecular architecture by the degree of deprotonation: self-assembled di- and tetranuclear copper(II) complexes of *N*,*N*'-bis(2-pyridylmethyl)pyrazine-2,3-dicarboxamide

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## **Experimental section:**

**General:** Elemental analyses (C, H, N) were performed by the Campbell Microanalytical Laboratory, University of Otago. Infrared spectra were recorded on a Perkin Elmer Spectrum BX FT-IR System spectrometer. UV/VIS spectra were recorded on a Varian Cary 500 Scan UV-Vis-NIR Spectrophotometer. Molar conductivities were measured with a Suntex SC-170 conductivity meter.

1: To a solution of *N*,*N*'-bis(2-pyridylmethyl)pyrazine-2,3-dicarboxamide<sup>8</sup> (H<sub>2</sub>L, 80 mg, 230 μmol) in acetonitrile (15 ml) was added a solution of copper(II) tetrafluoroborate tetrahydrate (71 mg, 230 μmol) in acetonitrile (10 ml) and the resulting dark navy-blue solution was stirred at room temperature for four hours. With diethyl ether vapour diffusion into the reaction mixture 97 mg (77 μmol, 67 %) of  $[Cu^{II}(H_2L)(MeCN)]_2(BF_4)_4$  (1) was obtained as a navy-blue crystalline solid. Elemental analysis calcd. (%) for  $[Cu^{II}(H_2L)(MeCN)]_2(BF_4)_4$ ,  $C_{40}H_{38}B_4N_{14}O_4F_{16}Cu_2$  (1253.16 g mol<sup>-1</sup>): C 38.34, H 3.06, N 15.65; found: C 38.33, H 2.99, N 15.37; IR (KBr, disk): v~ (cm<sup>-1</sup>) = 3422, 3058, 2924, 1641, 1615, 1564, 1534, 1468, 1446, 1419, 1386, 1306, 1286, 1212, 1123, 1083, 1032, 929, 880, 771, 721, 668, 627, 533, 521, 462; ESI-MS (MeCN): *m*/*z* (fragment) = 410 ( $[Cu^{II}(HL)]^+$ ), 349 ( $[H_3L]^+$ ), 226 ( $[Cu^{II}(H_2L)(MeCN)]^{2+}$ ; UV/VIS (MeCN):  $\lambda_{max}$  (ε) = 262 (49500), 600 nm (299 M<sup>-1</sup> cm<sup>-1</sup>);  $\Lambda_m$ (MeCN) = 576 mol<sup>-1</sup> cm<sup>2</sup> Ω<sup>-1</sup>.

Crystal data for 1: C<sub>20</sub>H<sub>19</sub>B<sub>2</sub>CuF<sub>8</sub>N<sub>7</sub>O<sub>2</sub>,  $M_r = 626.58$ , blue plate (0.40 x 0.35 x 0.02 mm<sup>3</sup>), triclinic, space group *P*-1, *a* = 10.5129(3), *b* = 10.7093(3), *c* = 11.9977(3) Å,  $\alpha = 87.8400(10)$ ,  $\beta = 74.2720(10)$ ,  $\gamma = 72.5870(10)^\circ$ , V = 1239.22(6) Å<sup>3</sup>, Z = 2,  $\rho_{calcd} = 1.679$  g cm<sup>-3</sup>, F(000) = 630, T = 150(2) K,  $\mu = 0.976$  mm<sup>-1</sup>, Mo<sub>Ka</sub> radiation ( $\lambda = 0.71073$  Å), Data were collected on a Bruker SMART diffractometer. A total of 11056 reflections were collected in the range  $2.54 < 2\theta < 50.80^\circ$ , and the 4480 [R(int) = 0.0201] independent reflections were used in the structural analysis. The structure was solved by direct methods (SHELXS-97)<sup>10</sup> and refined against all  $F^2$  data (SHELXL-97)<sup>11</sup> to RI = 0.0272 [for 4480  $I > 2 \sigma(I)$ ; wR2 = 0.0731 and GOF = 1.027 for all 4480  $F^2$ ; 370 parameters; all non-hydrogen atoms anisotropic; hydrogen atoms inserted at calculated positions and riding on the attached atom except for H(5) and H(6) which were located from a difference map and allowed to freely refine].

**2:** To a solution of *N*,*N*-bis(2-pyridylmethyl)pyrazine-2,3-dicarboxamide<sup>8</sup> (H<sub>2</sub>L, 120 mg, 345 µmol) in acetonitrile (30 ml) was added a solution of copper(II) tetrafluoroborate tetrahydrate (107 mg, 345 µmol) in acetonitrile (20 ml). The dark navy-blue solution was treated with triethyl amine (35 mg, 345 µmol), and the resulting grass-green solution was stirred at room temperature for four hours. With diethyl ether vapour diffusion into the reaction mixture, 120 mg (60 µmol, 70 %) of  $[Cu^{II}(HL)]_4(BF_4)_4$  (**2**) was obtained as shiny grass-green octahedral crystals. Strongly twinned crystals of **2**·3.5MeCN suitable for X-ray crystal structure determination were obtained by vapour diffusion of diethyl ether into a solution of **2** in acetonitrile. Elemental analysis calcd. (%) for  $[Cu^{II}(HL)]_4(BF_4)_4$ ,  $[C_{72}H_{60}B_4N_24O_8F_{16}Cu_4]$ 

(1990.82 g mol<sup>-1</sup>): C 43.44, H 3.04, N 16.89; found: C 43.18, H 3.33, N 16.72; IR (KBr, disk): v~ (cm<sup>-1</sup>) = 3456, 1651, 1482, 1438, 1386, 1315, 1287, 1211, 1124, 1083, 1035, 762, 612, 533, 521; ESI-MS (MeCN): m/z (fragment) = 908 ({[Cu<sup>II</sup><sub>4</sub>(HL)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub><sup>2+</sup>), 820 ([Cu<sup>II</sup><sub>4</sub>(L)<sub>2</sub>(HL)<sub>2</sub>]<sup>2+</sup>), 615.5 ([Cu<sup>II</sup><sub>6</sub>(L)<sub>2</sub>(HL)<sub>4</sub>]<sup>4+</sup>), 576.3 ({[Cu<sup>II</sup><sub>4</sub>(HL)<sub>4</sub>](BF<sub>4</sub>)}<sup>3+</sup>), 410.5 ([Cu<sup>II</sup><sub>4</sub>(HL)<sub>4</sub>]<sup>4+</sup>), 349 ([H<sub>3</sub>L]<sup>+</sup>); UV/VIS (MeCN):  $\lambda_{max}$  ( $\epsilon$ ) = 262 (72500), 699 (331), 1290 (195 M<sup>-1</sup> cm<sup>-1</sup>);  $\Lambda_m$ (MeCN) = 440 mol<sup>-1</sup> cm<sup>2</sup>  $\Omega^{-1}$ .

Crystal data for 2·3.5MeCN:  $C_{79}H_{60}B_4Cu_4F_{16}N_{27.5}O_8$ ,  $M_r = 2123.95$ , green block (0.42) x 0.36 x 0.20 mm<sup>3</sup>), monoclinic, space group Cc, a = 21.4502(5), b = 21.4616(5), c = 21.4616(5)19.9220(5) Å,  $\beta = 90.156(2)^{\circ}$ , V = 9171.2(4) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.538$  g cm<sup>-3</sup>, F(000) = 4282, T = 200(2) K,  $\mu$  = 1.017 mm<sup>-1</sup>, Mo<sub>Ka</sub> radiation ( $\lambda$  = 0.71073 Å). Data were collected on a Bruker SMART diffractometer. A total of 21082 reflections were collected in the range  $4.08 < 2\theta < 52.96^{\circ}$ , and the 15580 [R(int) = 0.0741] independent reflections were used in the structural analysis. The structure was solved by direct methods  $(SHELXS-97)^{10}$  and refined against all  $F^2$  data  $(SHELXL-97)^{11}$  to RI = 0.0603 [for 8779  $I > 2 \sigma(I)$ ; wR2 = 0.1366 and GOF = 0.909 for all 15580  $F^2$ ; 1314 parameters: all non-hydrogen atoms anisotropic except the 7 half occupancy MeCN molecules; hydrogen atoms inserted at calculated positions and riding on the attached atom, except for H(2a), H(4a), H(6a) and H(8a) which were fixed symmetrically between the two amide oxygen atoms; no hydrogen atoms were inserted on the 7 half occupancy MeCN molecules]. The structure was tetragonally twinned [twin law:  $0 \ 1 \ 0 \ / \ -1 \ 0 \ 0 \ / \ 0 \ 0 \ -1$ ; twin components:  $0.184(2), \ 0.122(2),$ 0.312(2); Flack parameter = -0.025(14), necessitating imposition of 4mm symmetry restraints on bond distances].

Crystal data for 2.3MeCN (different space group to that observed for 2.3.5MeCN):  $C_{79}H_{70.5}B_4Cu_4F_{16}N_{27.5}O_8$ ,  $M_r = 2134.53$ , green plate (0.38 x 0.35 x 0.22 mm<sup>3</sup>), monoclinic, space group P2(1), a = 15.189(3), b = 15.191(3), c = 20.048(4) Å,  $\beta =$ 90.41(3)°,  $V = 4625.8(16) \text{ Å}^3$ , Z = 2,  $\rho_{\text{calcd.}} = 1.518 \text{ g cm}^{-3}$ , F(000) = 2140, T = 200(2)K,  $\mu = 1.007$  mm<sup>-1</sup>. Data were collected on a Stoe IPDS II image-plate diffractometer, using graphite-monochromatised Mo<sub>Ka</sub> radiation ( $\lambda = 0.71073$  Å) from a rotatinganode generator. A total of 24008 reflections were collected in the range  $8.48 < 2\theta <$ 49.42°, and the 15222 [R(int) = 0.0575] independent reflections were used in the structural analysis. The structure was solved by direct methods (SHELXS-97)<sup>10</sup> and refined against all  $F^2$  data (SHELXL-97)<sup>11</sup> to RI = 0.0800 (for 12059  $I > 2 \sigma(I)$ ; wR2= 0.2204 and GOF = 1.025 for all 15222  $F^2$ ; 1290 parameters; all non-hydrogen atoms anisotropic; hydrogen atoms inserted at calculated positions and riding on the attached atom, except for H(12), H(34), H(56) and H(78) which were fixed symmetrically between the two amide oxygen atoms. The structure was tetragonally twinned [twin law:  $0 \ 1 \ 0 \ / \ -1 \ 0 \ 0 \ / \ 0 \ 0 \ -1$ ; twin components:  $0.229(2), \ 0.066(2),$ 0.216(2); Flack parameter = -0.010(23), necessitating imposition of 4mm symmetry restraints on bond distances].



Molecular structure of the monoclinic tetragonally twinned  $[Cu^{II}(HL)]_4^{4+}$ , the cation of complex 2·3MeCN. Hydrogen atoms, except H(12), H(34), H(56) and H(78), have been omitted for clarity.

- 8 10 J. Hausmann and S. Brooker, unpublished results.
- G. M. Sheldrick, Acta Crystallogr., Sect. A, 1990, 46, 467; G. M. Sheldrick, Methods Enzymol., 1997, 276, 628.
- 11 G. M. Sheldrick and T. R. Schneider, Methods Enzymol., 1997, 277, 319



Figure S1. Treatment of 1 in acetonitrile solution with one equivalent of DABCO, added in four equal portions, to form 2.