Supplementary Material (ESI) for New Journal of Chemistry


# Supplementary Information

## Reinvestigation of the spin crossover phenomenon in the ferrous complex $[Fe(HB(pz)_3)_2]$

Lionel Salmon,[a,b*] Gábor Molnár,[a,b] Saioa Cobo,[a,b] Pascal Oulié,[a,b] Michel Etienne,[a,b] Tarik Mahfoud,[a,b,c] Philippe Demont,[d] Akira Eguchi,[e] Hiroshi Watanabe,[e] Koichiro Tanaka[e] and Azzedine Bousseksou[a,b*]

[a] *CNRS, Laboratoire de Chimie de Coordination, 205 route de Narbonne, Toulouse, France*
[b] *Université de Toulouse, UPS, INPT, LCC, 31077 Toulouse, France*
[c] *School of Science and Engineering, Al Akhawayn University in Ifrane, 53000 Ifrane, Morocco*
[d] *Laboratoire de Physique des Polymères-CIRIMAT, CNRS UMR-5085 Université Toulouse III, 118 Route de Narbonne, 31062 Toulouse Cedex, France*
[e] *Department of Physics, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan*

**Figure S1.** Photographs showing the temperature dependence of the color of the "as prepared" microcystalline sample $[Fe(HB(pz)_3)_2]$ at 295 K (**a**) and at 470 K (**b**) as well as after the first thermal cycle at 295 K (**c**). Microscope images recorded at 295 K displaying the typical aspect of the same sample before (**d**, **e**) and after (**f**, **g**) the first thermal cycle.

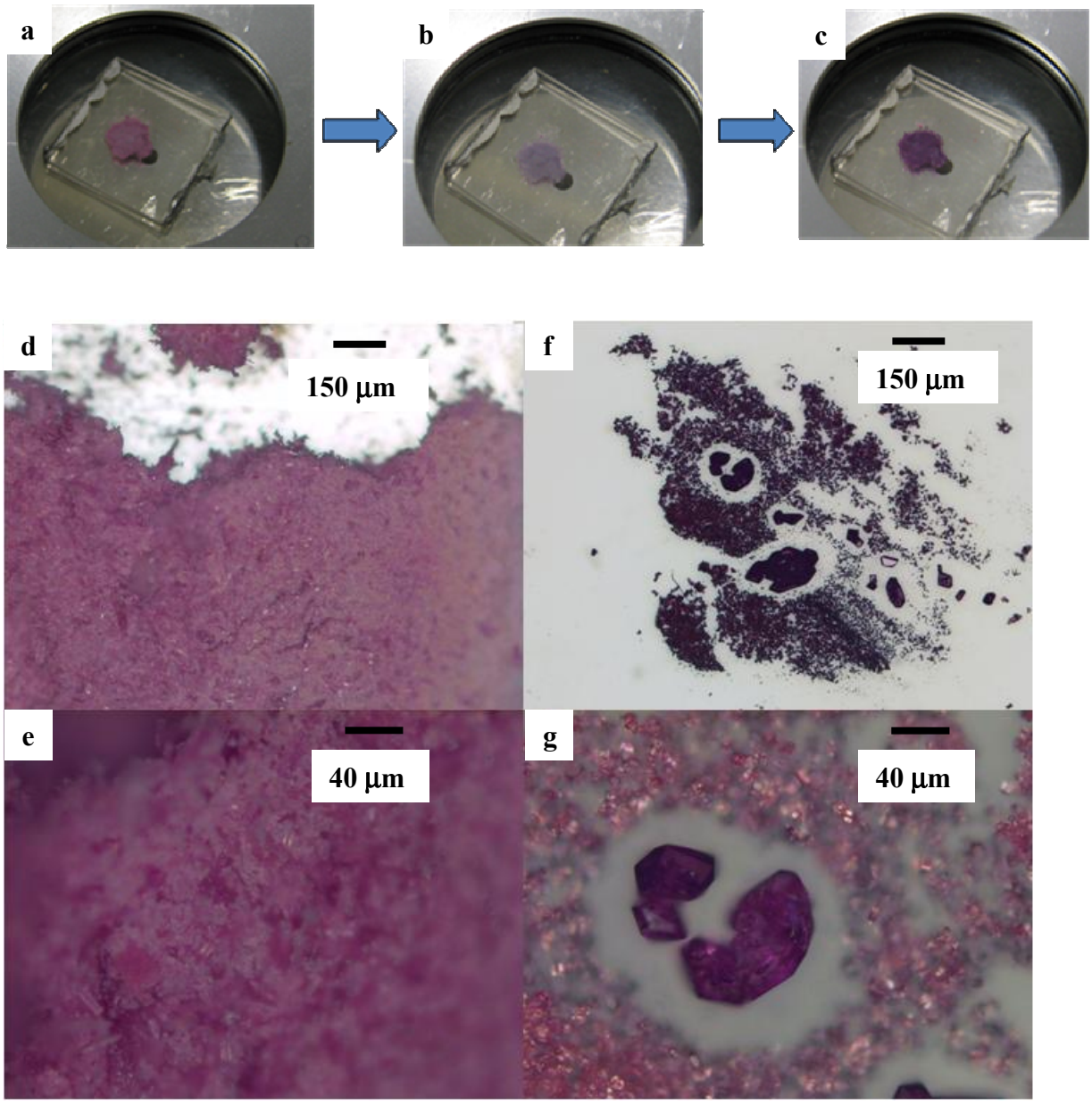


**Figure S2.** Digital images recorded in-situ during the first heating cycle of **1**.

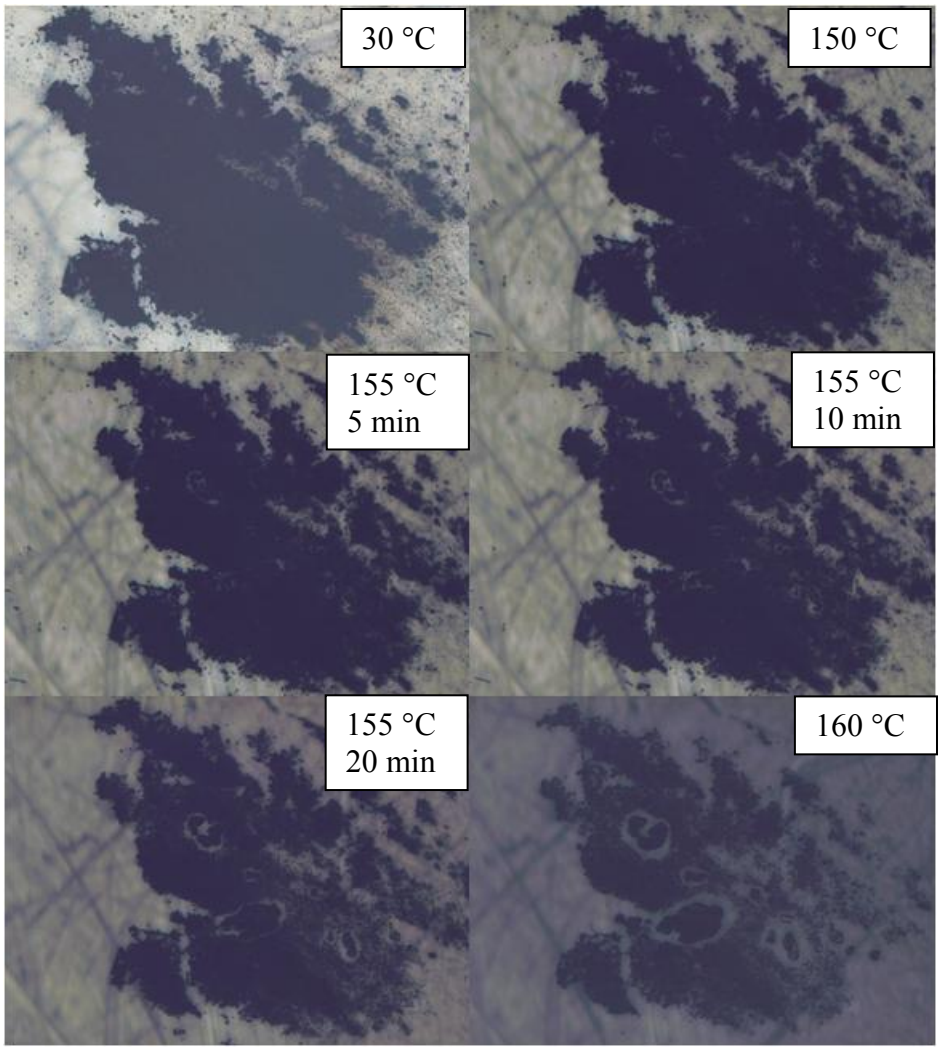
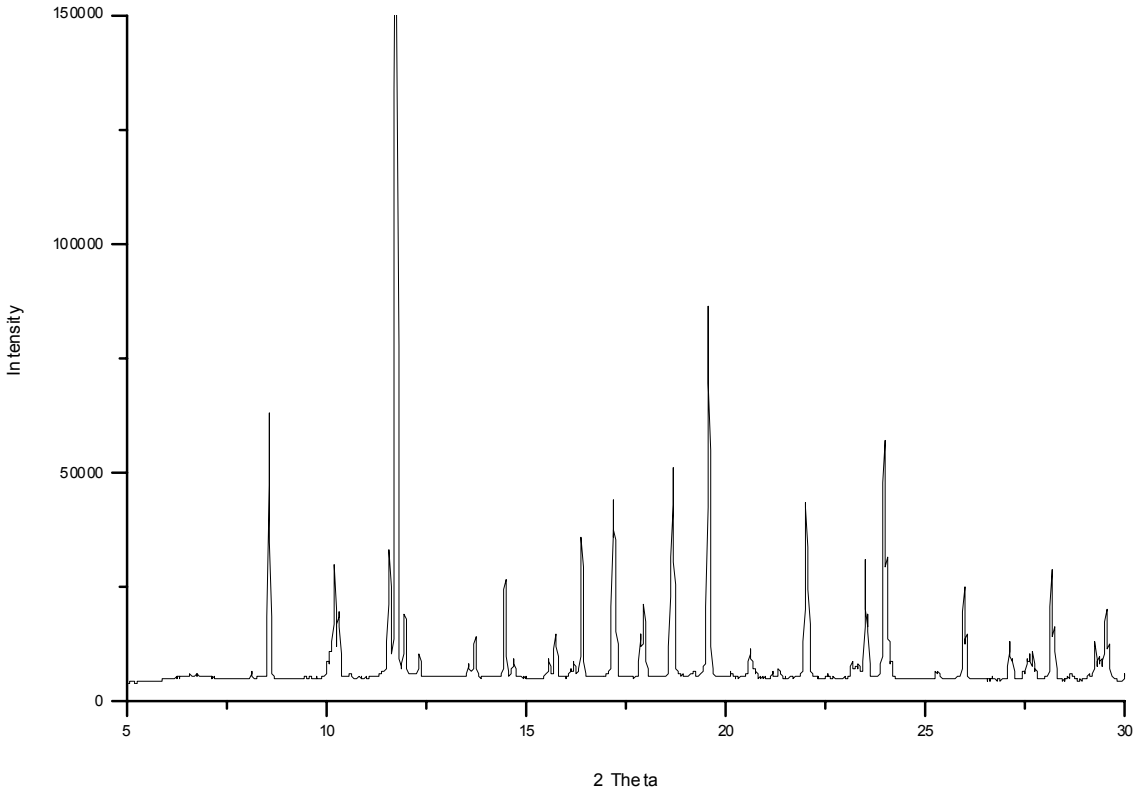


**Figure S3. (a)** Powder X-ray diffractogram of **1** acquired at 298 K following the first thermal cycle. **(b)** Powder X-ray diffractogram of **1** calculated from single crystal X-ray data (293 K).

**a)**




**b)**

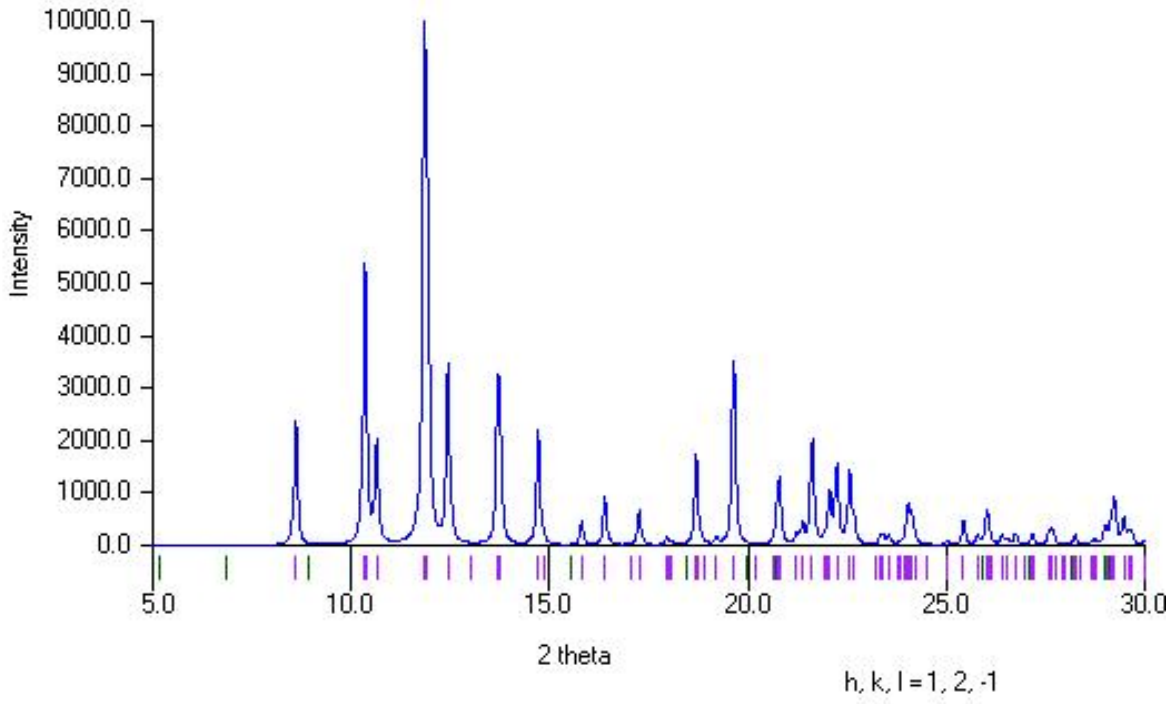


**Table S1.** Bond distances (Å) for **1** determined at 298 K and 420 K from single crystal diffraction data

| | | | **298 K** | **420 K** |
|---|---|---|---|---|
| Fe(1) | - | N(12) | 1.980(3) | 2.095(4) |
| Fe(1) | - | N(22) | 1.987(3) | 2.097(3) |
| Fe(1) | - | N(32) | 1.980(4) | 2.099(5) |
| Fe(1) | - | N(41) | 1.974(4) | 2.091(5) |
| Fe(1) | - | N(51) | 1.992(3) | 2.113(3) |
| Fe(1) | - | N(61) | 1.976(3) | 2.094(4) |
| N(11) | - | N(12) | 1.371(4) | 1.362(5) |
| N(11) | - | C(11) | 1.349(5) | 1.341(7) |
| N(11) | - | B(1) | 1.540(5) | 1.533(7) |
| N(12) | - | C(13) | 1.335(5) | 1.334(6) |
| N(21) | - | N(22) | 1.373(3) | 1.369(5) |
| N(21) | - | C(21) | 1.346(5) | 1.337(6) |
| N(21) | - | B(1) | 1.536(5) | 1.533(7) |
| N(22) | - | C(23) | 1.335(5) | 1.341(5) |
| N(31) | - | N(32) | 1.369(4) | 1.361(5) |
| N(31) | - | C(31) | 1.343(6) | 1.344(8) |
| N(31) | - | B(1) | 1.527(6) | 1.544(8) |
| N(32) | - | C(33) | 1.334(6) | 1.332(8) |
| N(41) | - | N(42) | 1.369(4) | 1.363(5) |
| N(41) | - | C(41) | 1.331(6) | 1.328(9) |
| N(42) | - | C(43) | 1.346(6) | 1.345(9) |
| N(42) | - | B(2) | 1.531(6) | 1.527(9) |
| N(51) | - | N(52) | 1.367(4) | 1.361(5) |
| N(51) | - | C(51) | 1.330(5) | 1.339(6) |
| N(52) | - | C(53) | 1.351(5) | 1.345(6) |
| N(52) | - | B(2) | 1.535(5) | 1.536(7) |
| N(61) | - | N(62) | 1.367(4) | 1.366(5) |
| N(61) | - | C(61) | 1.332(5) | 1.333(7) |
| N(62) | - | C(63) | 1.345(4) | 1.340(7) |
| N(62) | - | B(2) | 1.535(5) | 1.529(7) |
| C(11) | - | C(12) | 1.364(6) | 1.366(8) |
| C(12) | - | C(13) | 1.381(5) | 1.368(7) |
| C(21) | - | C(22) | 1.377(5) | 1.361(7) |
| C(22) | - | C(23) | 1.380(5) | 1.369(7) |
| C(31) | - | C(32) | 1.372(6) | 1.369(9) |
| C(32) | - | C(33) | 1.379(6) | 1.362(9) |
| C(41) | - | C(42) | 1.394(6) | 1.394(9) |
| C(42) | - | C(43) | 1.363(6) | 1.343(9) |
| C(51) | - | C(52) | 1.387(5) | 1.380(8) |
| C(52) | - | C(53) | 1.356(5) | 1.355(8) |
| C(61) | - | C(62) | 1.388(5) | 1.388(10) |
| C(62) | - | C(63) | 1.360(5) | 1.340(9) |

**Table S2.** Bond angles (deg) for **1** determined at 298 K and 420 K from single crystal diffraction data

| | | | | | | **298 K** | **420 K** |
|---|---|---|---|---|---|---|---|
| N(12) | - | Fe(1) | - | N(22) | | 88.33(11) | 86.53(14) |
| N(12) | - | Fe(1) | - | N(32) | | 89.05(12) | 86.34(15) |
| N(12) | - | Fe(1) | - | N(41) | | 91.67(12) | 92.67(15) |
| N(12) | - | Fe(1) | - | N(51) | | 92.68(11) | 94.62(14) |
| N(12) | - | Fe(1) | - | N(61) | | 179.01(12) | 177.96(16) |
| N(22) | - | Fe(1) | - | N(32) | | 88.35(12) | 86.11(12) |
| N(22) | - | Fe(1) | - | N(41) | | 92.25(12) | 96.01(14) |
| N(22) | - | Fe(1) | - | N(51) | | 177.97(12) | 177.13(12) |
| N(22) | - | Fe(1) | - | N(61) | | 90.88(11) | 92.37(14) |
| N(32) | - | Fe(1) | - | N(41) | | 179.07(13) | 177.60(14) |
| N(32) | - | Fe(1) | - | N(51) | | 89.91(12) | 91.33(12) |
| N(32) | - | Fe(1) | - | N(61) | | 91.53(12) | 95.30(15) |
| N(41) | - | Fe(1) | - | N(51) | | 89.48(12) | 86.57(14) |
| N(41) | - | Fe(1) | - | N(61) | | 87.75(12) | 85.74(15) |
| N(51) | - | Fe(1) | - | N(61) | | 88.12(11) | 86.56(14) |
| N(12) | - | N(11) | - | C(11) | | 109.1(3) | 109.5(4) |
| N(12) | - | N(11) | - | B(1) | | 118.0(2) | 119.6(4) |
| C(11) | - | N(11) | - | B(1) | | 132.7(3) | 130.7(4) |
| Fe(1) | - | N(12) | - | N(11) | | 119.3(2) | 118.6(3) |
| Fe(1) | - | N(12) | - | C(13) | | 134.3(2) | 135.7(3) |
| N(11) | - | N(12) | - | C(13) | | 106.0(3) | 105.4(4) |
| N(22) | - | N(21) | - | C(21) | | 109.6(3) | 109.6(3) |
| N(22) | - | N(21) | - | B(1) | | 118.4(2) | 119.1(4) |
| C(21) | - | N(21) | - | B(1) | | 132.0(3) | 131.3(4) |
| Fe(1) | - | N(22) | - | N(21) | | 118.74(19) | 118.7(2) |
| Fe(1) | - | N(22) | - | C(23) | | 135.5(2) | 135.9(3) |
| N(21) | - | N(22) | - | C(23) | | 105.7(3) | 105.3(3) |
| N(32) | - | N(31) | - | C(31) | | 109.5(3) | 109.5(4) |
| N(32) | - | N(31) | - | B(1) | | 117.7(3) | 118.8(4) |
| C(31) | - | N(31) | - | B(1) | | 132.7(3) | 131.6(4) |
| Fe(1) | - | N(32) | - | N(31) | | 119.8(3) | 119.1(4) |
| Fe(1) | - | N(32) | - | C(33) | | 134.2(2) | 135.2(3) |
| N(31) | - | N(32) | - | C(33) | | 105.9(3) | 105.6(4) |
| Fe(1) | - | N(41) | - | N(42) | | 119.1(3) | 119.1(4) |
| Fe(1) | - | N(41) | - | C(41) | | 134.9(2) | 134.9(3) |
| N(42) | - | N(41) | - | C(41) | | 106.0(3) | 105.9(5) |
| N(41) | - | N(42) | - | C(43) | | 108.9(3) | 108.7(5) |
| N(41) | - | N(42) | - | B(2) | | 118.6(3) | 118.8(5) |
| C(43) | - | N(42) | - | B(2) | | 132.3(3) | 132.4(4) |
| Fe(1) | - | N(51) | - | N(52) | | 119.2(2) | 118.2(2) |
| Fe(1) | - | N(51) | - | C(51) | | 134.2(2) | 135.5(3) |
| N(52) | - | N(51) | - | C(51) | | 106.1(3) | 105.7(3) |
| N(51) | - | N(52) | - | C(53) | | 109.2(3) | 109.7(3) |
| N(51) | - | N(52) | - | B(2) | | 118.2(2) | 119.2(3) |
| C(53) | - | N(52) | - | B(2) | | 132.0(3) | 130.7(4) |
| Fe(1) | - | N(61) | - | N(62) | | 119.9(2) | 118.6(3) |
| Fe(1) | - | N(61) | - | C(61) | | 134.2(2) | 136.0(4) |
| N(62) | - | N(61) | - | C(61) | | 105.8(3) | 105.3(4) |
| N(61) | - | N(62) | - | C(63) | | 109.8(3) | 108.9(4) |
| N(61) | - | N(62) | - | B(2) | | 117.7(2) | 119.1(4) |
| C(63) | - | N(62) | - | B(2) | | 132.5(3) | 131.9(4) |
| N(11) | - | C(11) | - | C(12) | | 108.8(3) | 108.8(5) |
| C(11) | - | C(12) | - | C(13) | | 105.1(4) | 104.6(5) |
| N(12) | - | C(13) | - | C(12) | | 110.9(3) | 111.7(5) |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| N(21) | - | C(21) | - | C(22) | | 108.5(3) | | 108.7(4) | | |
| C(21) | - | C(22) | - | C(23) | | 104.9(3) | | 105.3(4) | | |
| N(22) | - | C(23) | - | C(22) | | 111.3(3) | | 111.0(3) | | |
| N(31) | - | C(31) | - | C(32) | | 108.6(3) | | 108.3(5) | | |
| C(31) | - | C(32) | - | C(33) | | 105.0(4) | | 105.1(5) | | |
| N(32) | - | C(33) | - | C(32) | | 111.0(3) | | 111.5(5) | | |
| N(41) | - | C(41) | - | C(42) | | 111.3(3) | | 111.1(5) | | |
| C(41) | - | C(42) | - | C(43) | | 104.0(4) | | 104.1(6) | | |
| N(42) | - | C(43) | - | C(42) | | 109.7(3) | | 110.2(5) | | |
| N(51) | - | C(51) | - | C(52) | | 110.7(3) | | 110.5(5) | | |
| C(51) | - | C(52) | - | C(53) | | 105.3(3) | | 105.5(4) | | |
| N(52) | - | C(53) | - | C(52) | | 108.6(3) | | 108.5(4) | | |
| N(61) | - | C(61) | - | C(62) | | 110.7(3) | | 111.3(5) | | |
| C(61) | - | C(62) | - | C(63) | | 105.3(3) | | 104.2(5) | | |
| N(62) | - | C(63) | - | C(62) | | 108.5(3) | | 110.2(5) | | |
| N(11) | - | B(1) | - | N(21) | | 106.8(3) | | 109.1(4) | | |
| N(11) | - | B(1) | - | N(31) | | 109.1(3) | | 109.2(4) | | |
| N(21) | - | B(1) | - | N(31) | | 107.7(3) | | 108.0(4) | | |
| N(42) | - | B(2) | - | N(52) | | 108.2(3) | | 109.6(4) | | |
| N(42) | - | B(2) | - | N(62) | | 108.1(3) | | 109.7(4) | | |
| N(52) | - | B(2) | - | N(62) | | 106.8(3) | | 107.9(4) | | |

**Table S3.** Variation of the unit cell parameters of the powder sample of **1** during the first heating sequence

| | 298 K | 318 K | 338 K | 358 K | 378 K | 398 K | 413 K | variation |
|---|---|---|---|---|---|---|---|---|
| a (Å) | 17.11 | 17.11 | 17.166 | 17.190 | 17.242 | 17.31 | 17.37 | +1.520% |
| b (Å) | 17.11 | 17.11 | 17.166 | 17.190 | 17.242 | 17.31 | 17.37 | +1.520% |
| c (Å) | 7.493 | 7.496 | 7.520 | 7.544 | 7.565 | 7.563 | 7.567 | +0.988% |
| $\alpha$ (deg) | 90 | 90 | 90 | 90 | 90 | 90 | 90 | - |
| $\beta$ (deg) | 90 | 90 | 90 | 90 | 90 | 90 | 90 | - |
| $\gamma$ (deg) | 90 | 90 | 90 | 90 | 90 | 90 | 90 | - |
| V ($Å^3$) | 2194.4 | 2194.6 | 2216.0 | 2229.2 | 2249.0 | 2265.5 | 2282.6 | +4.019% |