Supplementary Data

Above Room Temperature Spin Crossover in Thioamide-Functionalised 2,6-bis(pyrazol-1-yl)pyridine Iron(II) Complexes.

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List of supplementary data

Synthesis and characterisation of bppCONH$_2$ and bppCONHMe

Synthesis and characterisation of $bppCONH_2$ and bppCONHMe

A solution of $SOCl_2$ (10 ml) and bppCOOH (0.893 g, 3.5 x 10^{-3} mols) was reacted at 75°C for 4 hrs under reflux. The condenser was capped with a $CaCl_2$ tube. Excess $SOCl_2$ was removed *in vacuo* and the resulting brown solid was dissolved in THF (25 ml). This solution was slowly added to conc. NH_4OH ($bppCONH_2$ synthesis) or NH_2Me (bppCONHMe synthesis) in ethanol (33%, 5 ml) while stirring. The solution was sealed and left stirring at room temperature for 2 hrs. The solution was concentrated to ca. 5 ml *in vacuo* giving a brown slurry which was filtered and washed with water yielding a white solid which was dried in a vacuum desiccator. The solid was dissolved in the minimum volume of boiling methanol and left in the freezer at -20°C giving white needle crystals.

$bppCONH_2$ Yield: 0.716 g, (88%). ^{1}H NMR (400 MHz, DMSO): δ 8.99 (d, *J* = 2.6 Hz, 2H), 8.57 (s, 1H), 8.22 (s, 2H), 7.92 (d, *J* = 7.3 Hz, 2H), 7.88 (s, 1H), 6.67 (dd, *J* = 2.4 Hz, *J* =1.8 Hz, 2H). ^{13}C NMR (400 MHz, DMSO): δ 165.62, 150.64, 148.41, 143.42, 128.84, 109.19, 107.55. MS (ESI, positive scan) *m/z* calculated = 255.0989 (M+H)+, 277.0808 (M+Na)+; Found = 255.0992 (M+H)+, 277.081 (M+Na)+.

bppCONHMe Yield: 0.797 g, (85%). ^{1}H NMR (400 MHz, DMSO): δ 9.09 (q, *J* = 4.3 Hz, 1H), 8.99 (d, *J* = 2.5 Hz, 2H), 8.21 (s, 2H), 7.92 (d, *J* = 1.1 Hz, 2H), 6.70 – 6.64 (m, 2H), 2.85 (d, *J* = 4.5 Hz, 3H). ^{13}C NMR (400 MHz, DMSO): δ 164.19, 150.66, 148.22, 143.45, 128.84, 109.21, 107.2, 26.95

NMR Ligand Characterisation

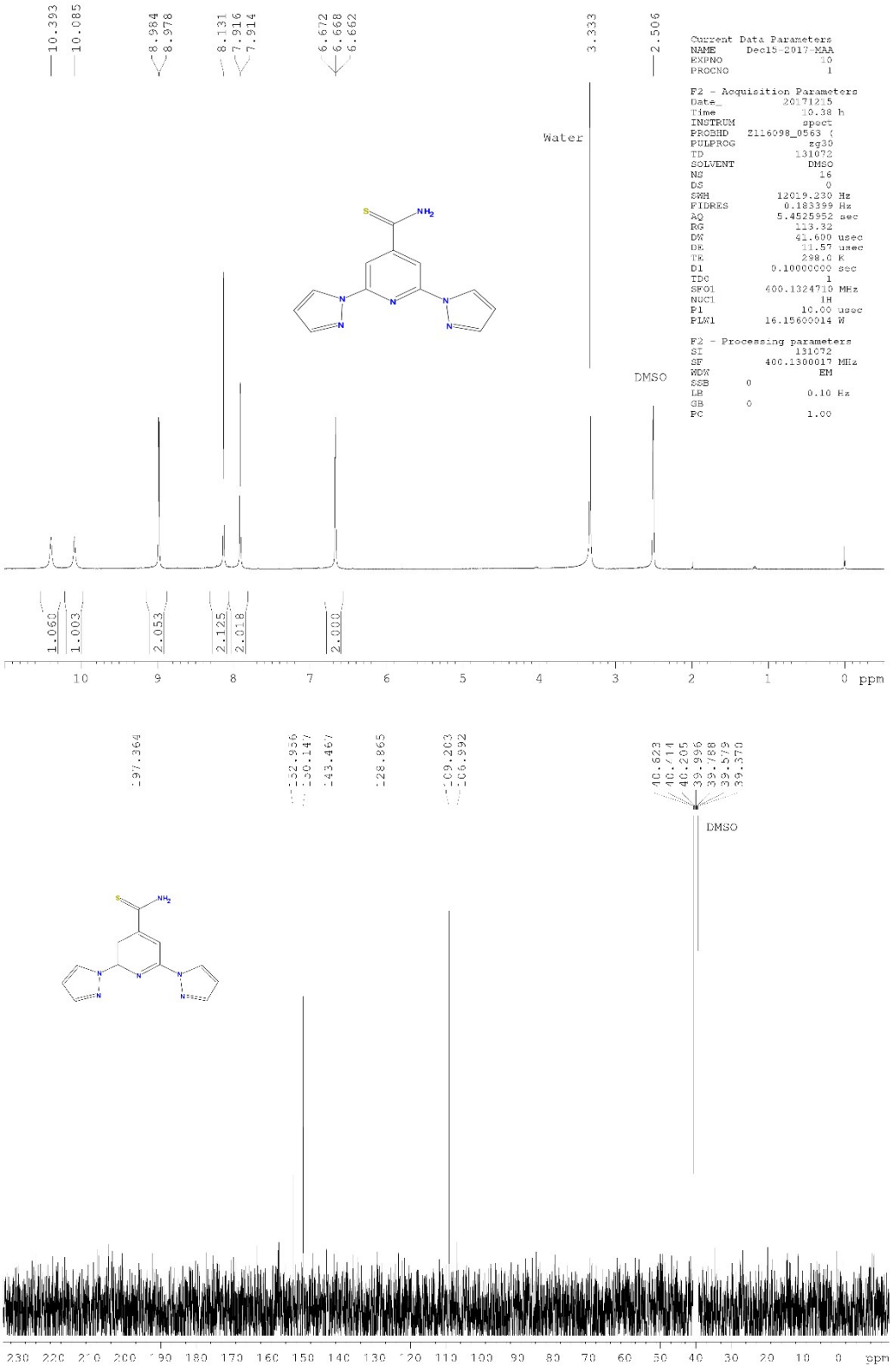

Figure.S1: ^{1}H NMR (top) and ^{13}C NMR (bottom) of **bppCSNH$_2$**.

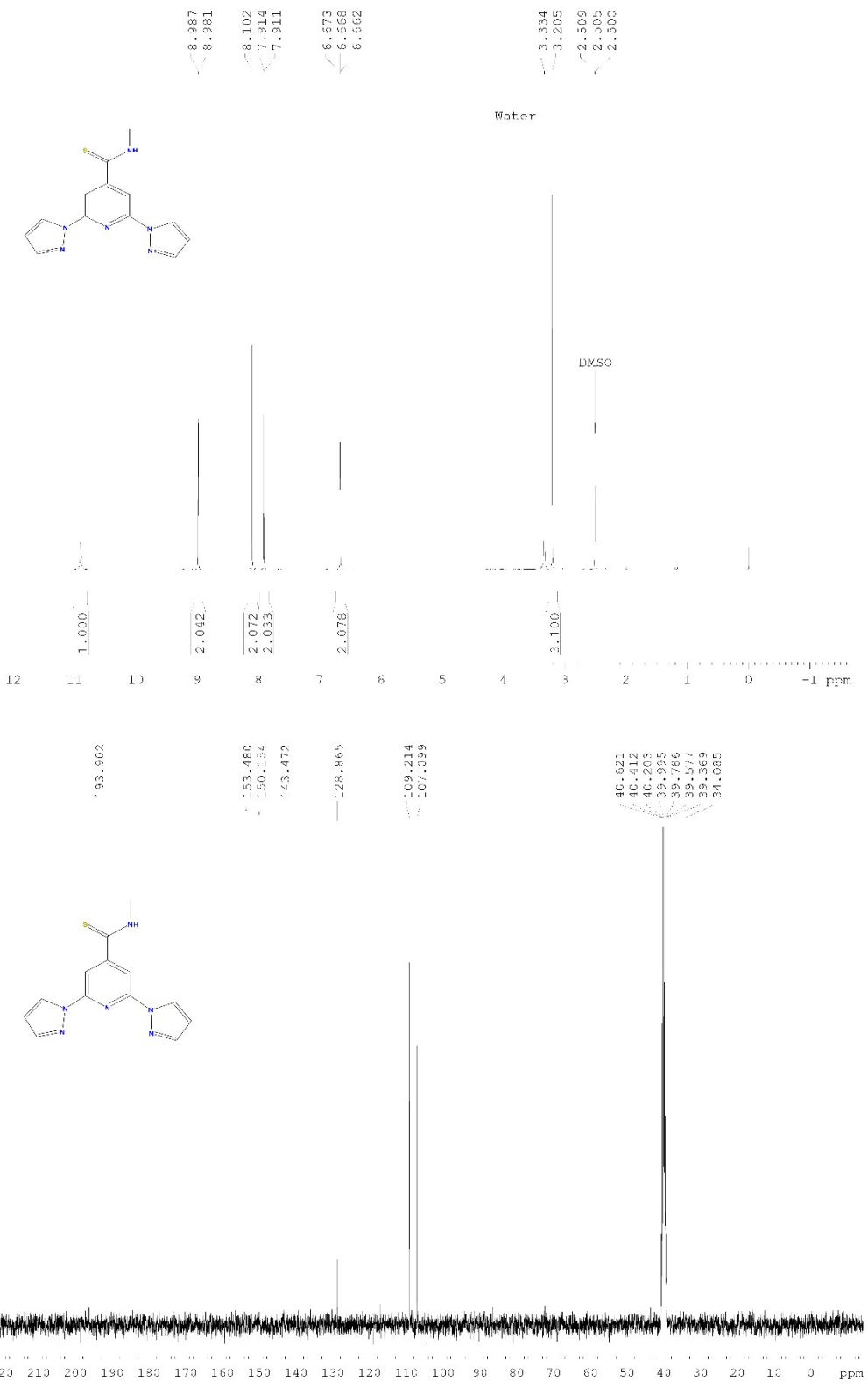

Figure.S2: ^{1}H NMR (top) and ^{13}C NMR (bottom) of **bppCSNHMe**.

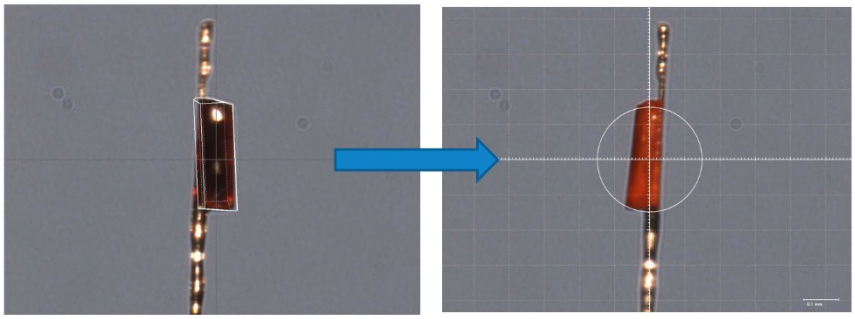

Figure.S3: Picture of XRD mounted crystal of [Fe(**bppCSNHMe**)$_2$](BF_4)$_2$.$MeNO_2$ taken at 330K (left) and 360K (right) showing change in colour and opacity due to irreversible loss of solvent.

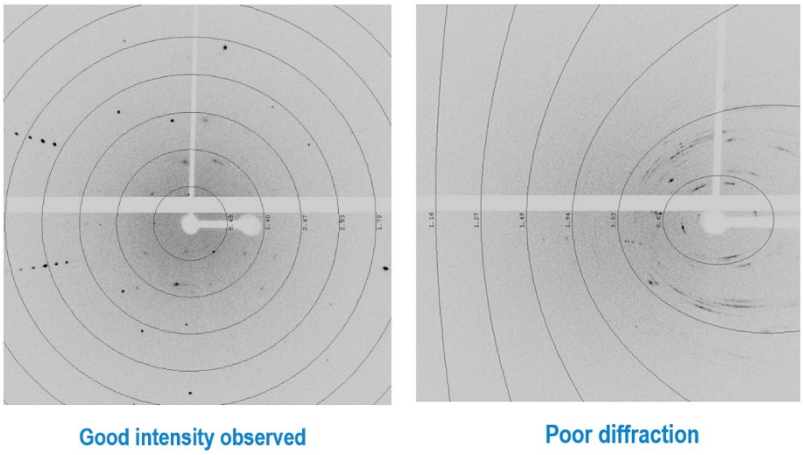

Figure.S4: Diffraction patterns for [Fe(**bppCSNHMe**)$_2$](BF_4)$_2$.$MeNO_2$ taken at 330K (left) and 360K (right) showing change in crystallinity.

TGA and DSC Thermal Analysis

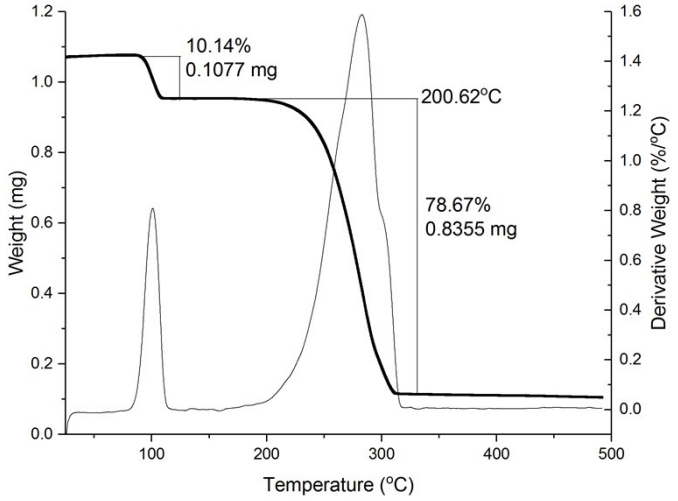

Figure.S5: TGA trace for [Fe(**bppCSNH$_2$**)$_2$](BF$_4$)$_2$.2MeNO$_2$

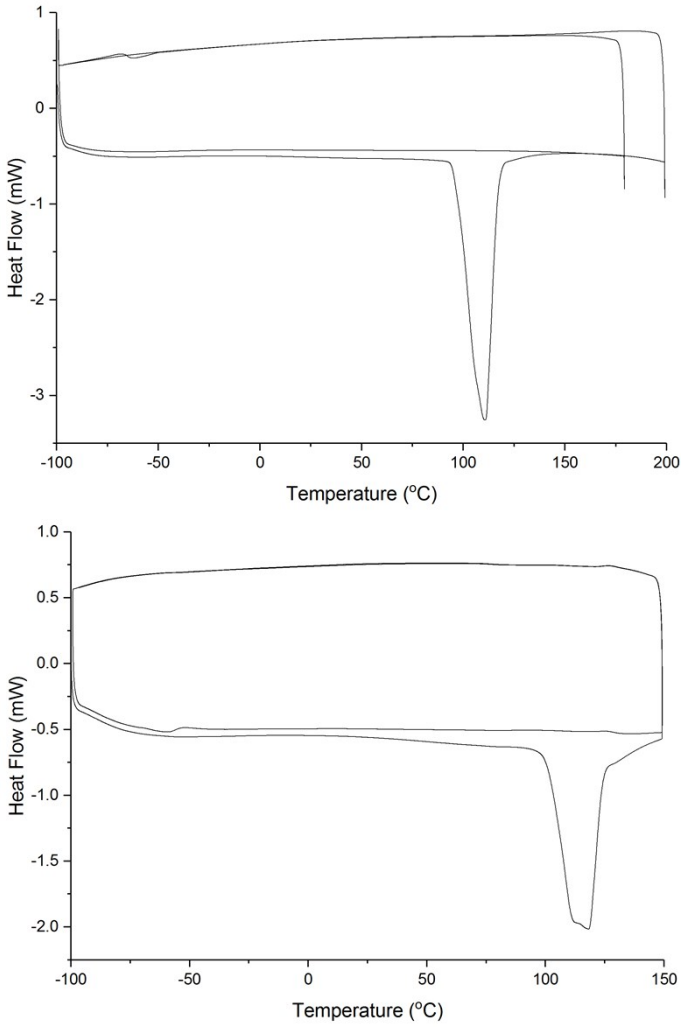

Figure.S6: DSC trace for [Fe(**bppCSNH$_2$**)$_2$](BF$_4$)$_2$.2MeNO$_2$ (top) and [Fe(**bppCSNH$_2$**)$_2$](ClO$_4$)$_2$.MeNO$_2$ (bottom), showing loss of solvent and no SCO

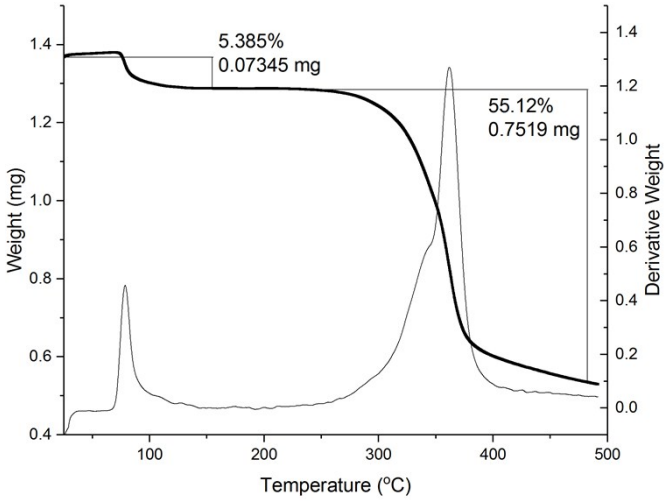

Figure.S7: TGA trace for [Fe(**bppCSNHMe**)$_2$]$(BF_4)_2$.0.5$MeNO_2$

Table S1: CCDC numbers for crystal structures submitted to Cambridge structural database

Compound	CCDC
bppCSNH$_2$	1860674
bppCSNHMe	1860675
[Fe(bppCSNH$_2$)$_2$](BF$_4$)$_2$.2MeNO$_2$ at 100 K	1860676
[Fe(bppCSNH$_2$)$_2$](BF$_4$)$_2$.2MeNO$_2$ at 290 K	1860677
[Fe(bppCSNHMe)$_2$](BF$_4$)$_2$.MeNO$_2$ at 100 K	1860678
[Fe(bppCSNHMe)$_2$](BF$_4$)$_2$.MeNO$_2$ at 290 K	1860679
[Fe(bppCSNHMe)$_2$](BF$_4$)$_2$.MeNO$_2$ at 330 K	1860680
[Fe(bppCSNHMe)$_2$](ClO$_4$)$_2$at 102 K	1860681
[Fe(bppCSNHMe)$_2$](ClO$_4$)$_2$at 290 K	1860682
[Fe(bppCSNHMe)$_2$](ClO$_4$)$_2$ at 370 K	1860683