

Supporting Information

Substituent dependence on the spin crossover behaviour of mononuclear Fe(II) complexes with asymmetric tridentate ligands

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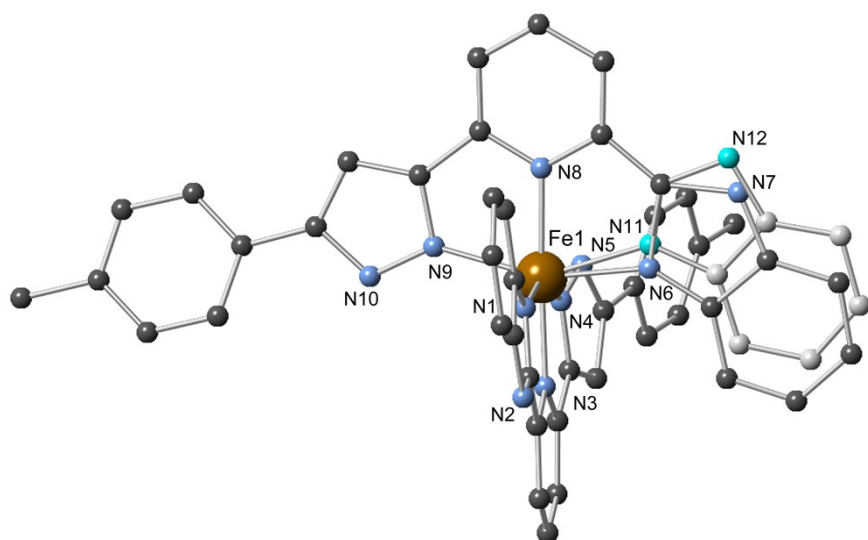


Figure S1. Molecular structure of **1'** at 100 K showing disorder of ligands.

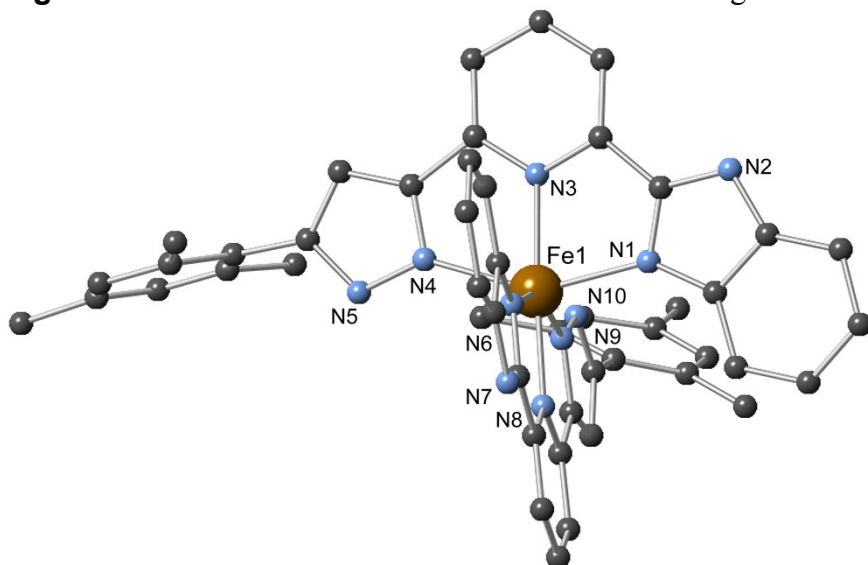


Figure S2. Molecular structure of **2'** at 100 K.

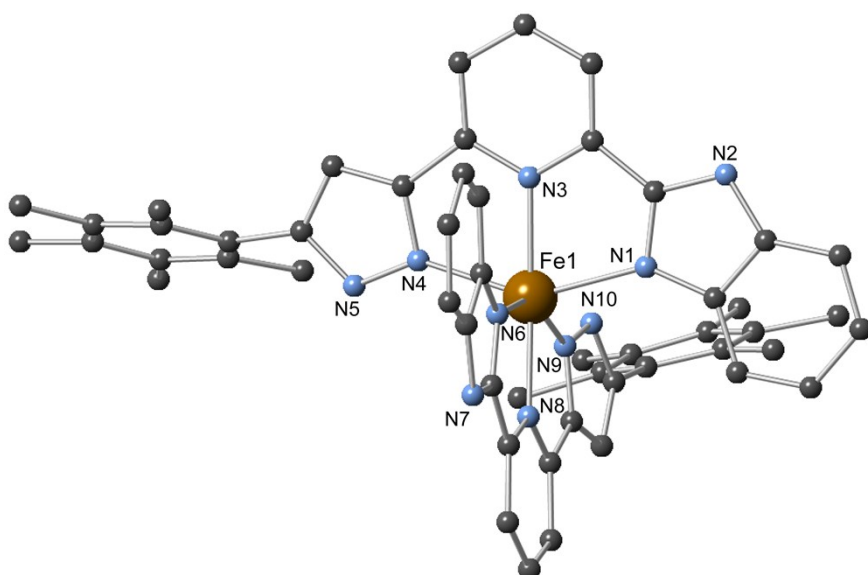


Figure S3. Molecular structure of **3'** at 100 K.

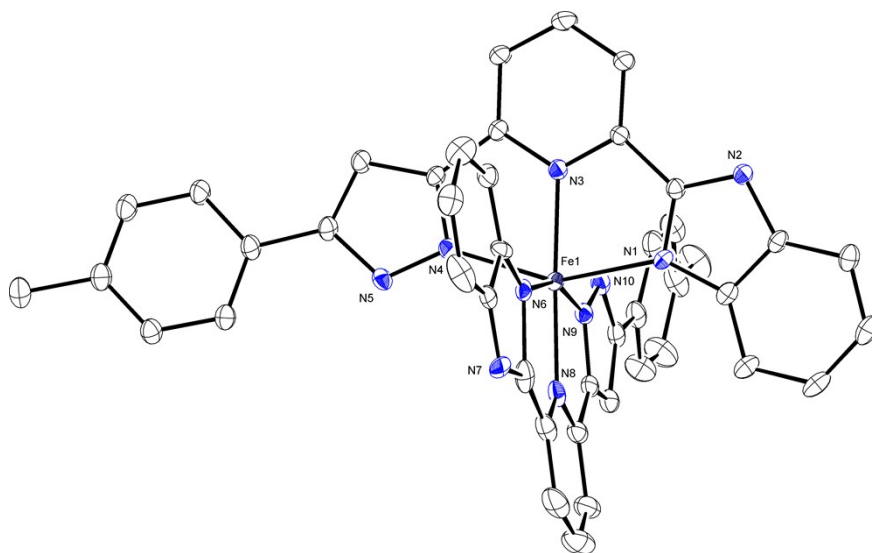


Figure S4. Molecular structure of **1'** at 100 K.

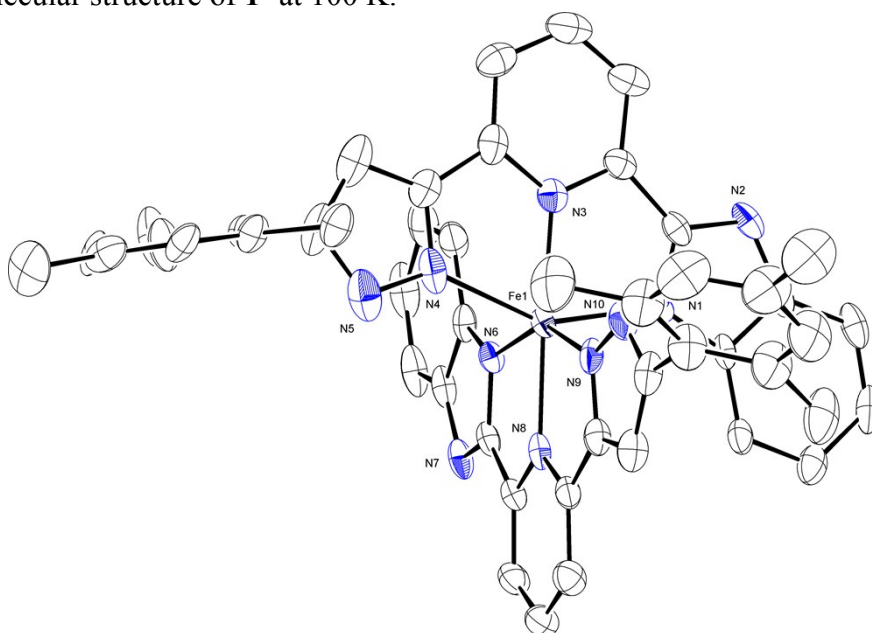


Figure S5. Molecular structure of **2'** at 100 K.

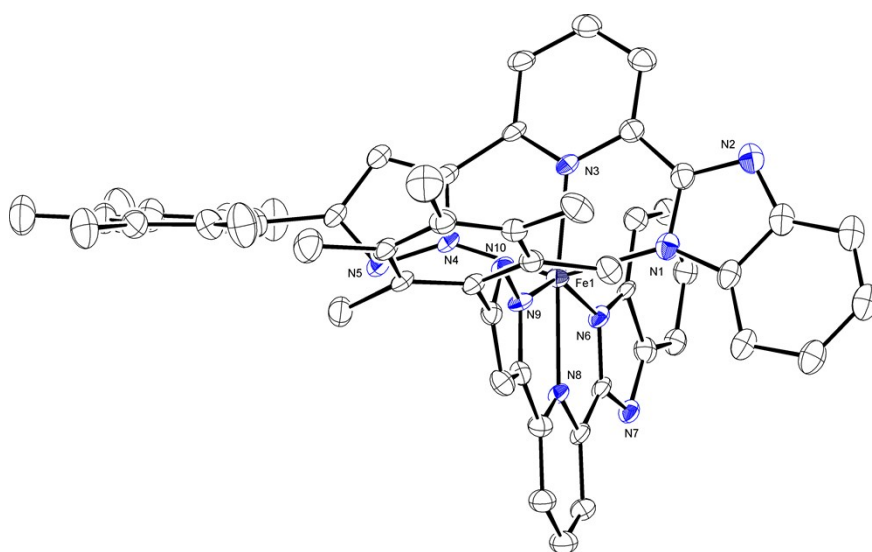


Figure S6. Molecular structure of **3'** at 100 K.

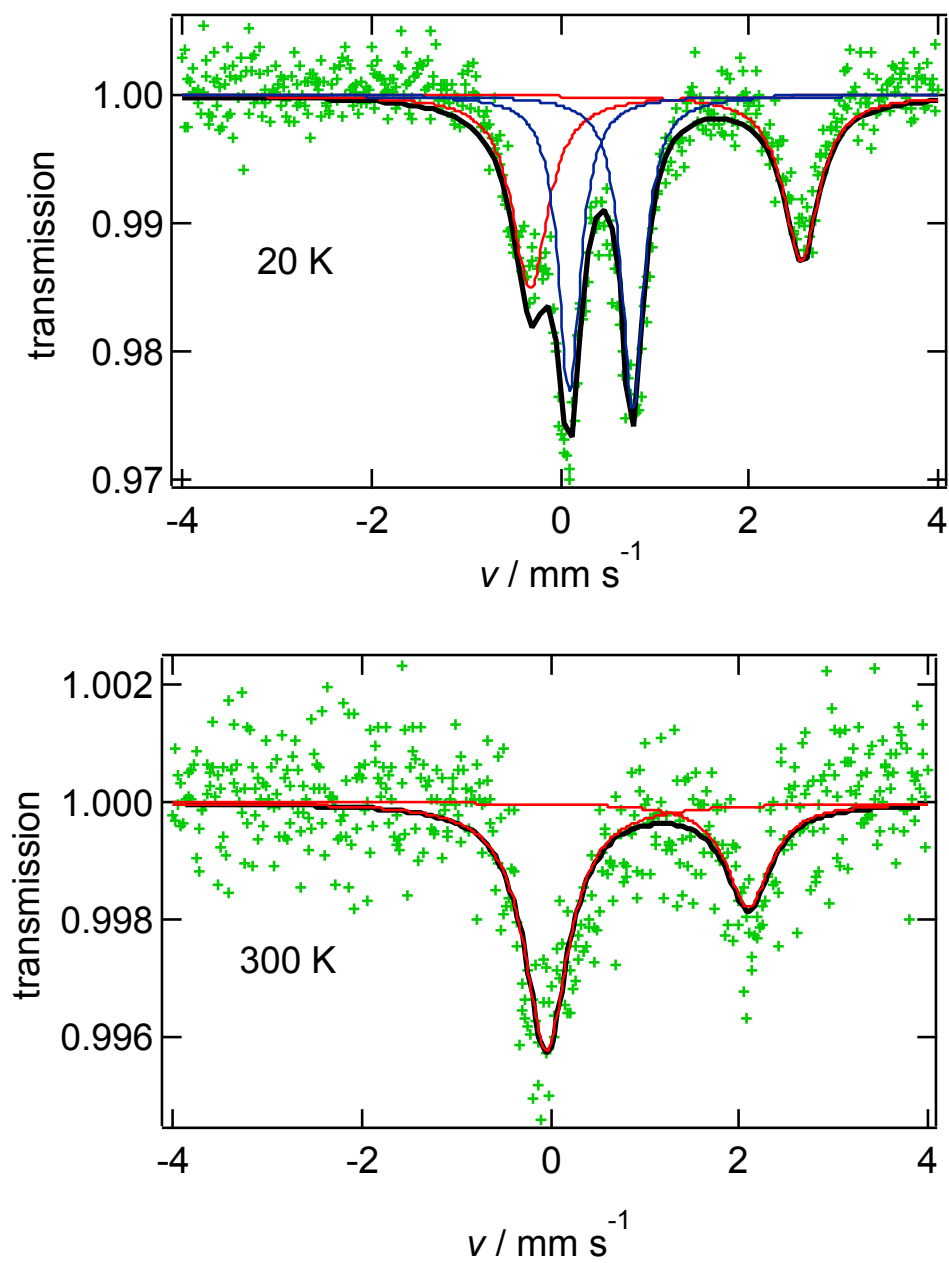


Figure S7. Mössbauer spectra of **1** at 20 K (top) and 300 K (bottom).

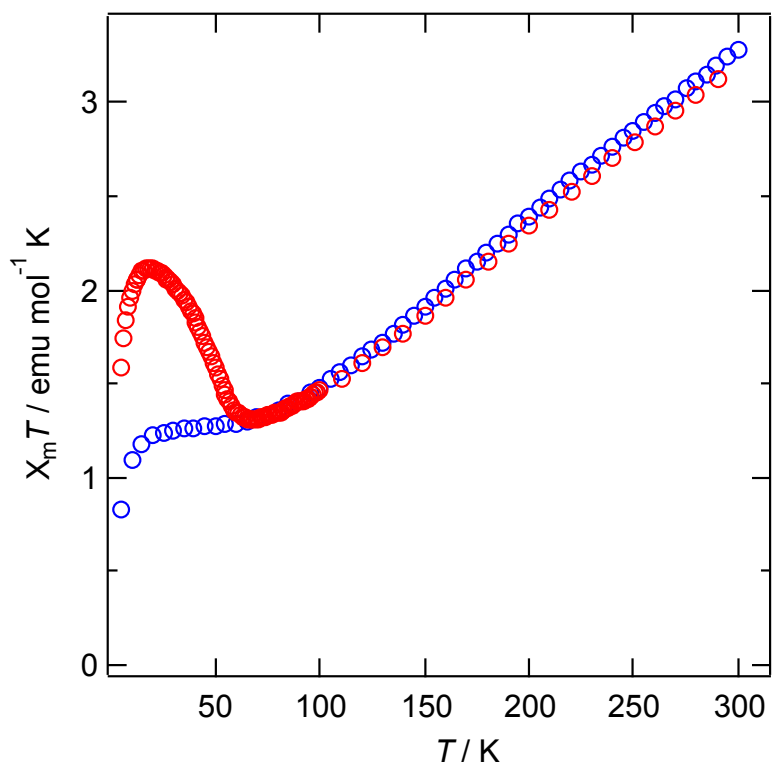


Figure S8. LIESST behavior of **1**.

Table S1. Crystal parameters of **1'**.

	20 K	100 K	270 K	LIESST
Formula	C ₅₂ H ₅₂ N ₁₀ O ₄ B ₂ F ₈ Fe	C ₅₂ H ₅₂ N ₁₀ O ₃ B ₂ F ₈ Fe	C ₅₂ H ₅₆ N ₁₀ O ₃ B ₂ F ₈ Fe	C ₅₂ H ₅₂ N ₁₀ O ₄ B ₂ F ₈ Fe
M / g mol ⁻¹	1110.50	1094.50	1098.53	1110.50
Temp. / K	20(2)	100(2)	100(2)	20(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> / Å	31.8358(9)	32.019(3)	32.372(12)	32.0647(13)
<i>b</i> / Å	16.2318(6)	16.3126(14)	16.452(6)	16.2520(5)
<i>c</i> / Å	24.1500(13)	24.246(2)	24.557(16)	24.1773(17)
α / °	-	-	-	-
β / °	121.0380(10)	121.2070(10)	121.401(4)	121.5440(10)
γ / °	-	-	-	-
<i>V</i> / Å ³	10692.8(8)	10831.7(16)	11164(9)	10737.5(9)
<i>Z</i>	8	8	8	8
<i>d</i> / g cm ⁻³	1.380	1.342	1.307	1.374
μ / mm ⁻¹	0.889	0.357	0.347	0.886
F(000)	4592	4528	4560	4592
Reflections				
collected / unique	18898 / 7220	31295 / 12376	32071 / 12718	21855 / 8554
<i>R</i> _{int}	0.2033	0.0603	0.0534	0.1017
GOF	1.092	1.022	1.030	1.219
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.1007	0.0858	0.0689	0.1189
<i>R</i> _w 2 (<i>I</i> > 2σ(<i>I</i>))	0.2814	0.2272	0.1892	0.3245
$\Delta\rho_{\max}$ / e Å ⁻³	1.101	1.842	0.875	1.481
$\Delta\rho_{\min}$ / e Å ⁻³	-0.704	-0.641	-0.497	-1.167
CCDC No.	1889870	1889871	1889872	1889873

Table S2. Crystal parameters of **2'** and **3'**.

	Comp. 2' (100 K)	Comp. 3' (100 K)
Formula	C _{53.5} H ₅₆ N ₁₀ O _{3.5} N ₁₀ B ₂ F ₈ Fe	C ₆₄ H ₇₈ N ₁₀ O ₂ B ₂ F ₈ Fe
M / g mol ⁻¹	1124.55	1248.83
Temp. / K	100(2)	100(2)
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> Error!	<i>P</i> 2 ₁ /n
<i>a</i> / Å	12.496(10)	18.389(3)
<i>b</i> / Å	12.836(10)	16.551(3)
<i>c</i> / Å	17.661(14)	22.333(3)
α / °	85.769(8)	-
β / °	73.318(11)	112.772(2)
γ / °	84.140(11)	-
<i>V</i> / Å ³	2696(4)	6267.2(16)
<i>Z</i>	2	4
<i>d</i> / g cm ⁻³	1.385	1.324
μ / mm ⁻¹	0.362	0.317
F(000)	1166	2624
Reflections		
collected / unique	12605 / 9703	34769 / 14330
<i>R</i> _{int}	0.0371	0.0767
GOF	1.069	1.252
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>))	0.1422	0.1335
<i>R</i> _w 2 (<i>I</i> > 2σ(<i>I</i>))	0.3343	0.2993
$\Delta\rho_{\max}$ / e Å ⁻³	2.092	2.498
$\Delta\rho_{\min}$ / e Å ⁻³	-0.923	-1.744
CCDC No.	1889874	1889875

Table S3. Mössbauer parameters for **1'** at 20 K.

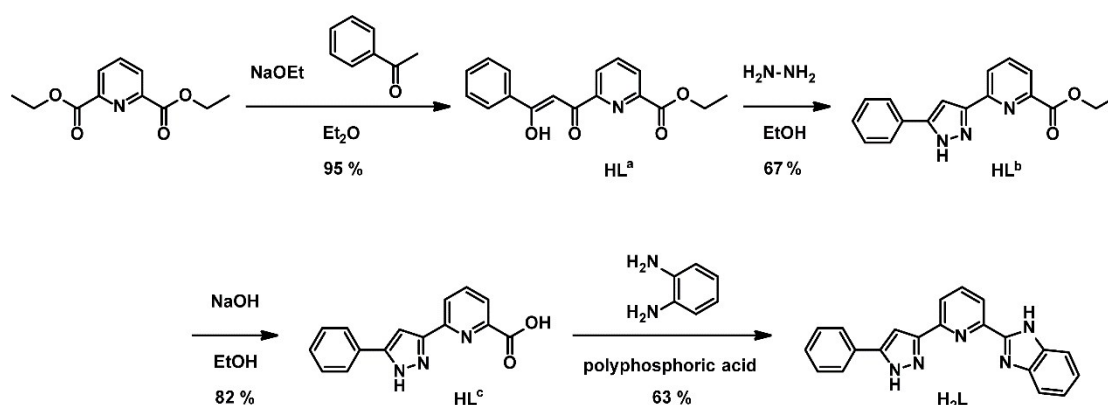
δ_{IS} (mm / s)	ΔE_Q (mm / s)	spin state	Area fraction (%)
0.435	0.670	Fe(II)LS	51.0
1.119	2.870	Fe(II)HS	49.0

Table S4. Mössbauer parameters for **1'** at 300 K.

δ_{IS} (mm / s)	ΔE_Q (mm / s)	spin state
1.028	2.140	Fe(II) HS

Syntheses of ligands

Non-substituted tridentate ligand, H_2L , was synthesized by the following procedure described in reference S1, which shown in Scheme S1. New Asymmetric tridentate ligands, H_2L^{1-3} , were synthesized following a protocol adapted from our previous study.^[S1] Recrystallization methods, yield and characterization data were described as follows.

**Scheme S1.** Synthetic pathway of H_2L .

Synthesis of 6-[1,3-dioxo-3-(2-phenyl)propionyl]pyridine-2-carboxylic acid ethyl ester (HL^a)^[S2]

A solution of Na (3.18 g, 138 mmol) in 150 ml ethanol was stirred at room temperature. After stirring, sodium ethoxide was obtained as white solid by evaporation. To this solid, a solution of acetophenone (13.46 g, 112 mmol) and diethyl-2,6-pyridinedicarboxylate (25.00 g, 112 mmol) in diethyl ether were then added. Yellow solid was obtained after 2 h reflux. The solid was separated by filtration, and carefully washed with ether. After drying, the solid was added to 200 ml water and 20 ml of acetic acid was added with stirring. After 24 h stirring, yellow solid was obtained by filtration. Last, the white solid HL^a was obtained by recrystallization from ethanol. (31.68 g, yield 95 %) 1H NMR (400 MHz, $CDCl_3$): δ 1.51 (t, 3H), 4.54 (q, 2H), 7.28 (s, 1H), 7.53 (t, 2H), 7.60 (t, 1H), 7.71 (s, 1H), 8.04 (t, 1H), 8.11 (d, 2H), 8.26 (d, 2H), 8.35 (d, 2H).

Synthesis of 6-[5-phenyl-1H-pyrazol-3-yl]-pyridine-2-carboxylic acid ethyl ester (HL^b)

A solution of hydrazine monohdrate (1.798 mL, 37.0 mmol) in 100 mL of ethanol was slowly added in a solution of HL^a (10 g, 33.6 mmol) in 300 mL of ethanol. The mixture was refluxed for 1 h. After refluxing, the yellow solution was obtained. The solution was evaporated to remove ethanol and brown oil was obtained. Brown oil was dissolved in dichloromethane, and washed by water to remove impurities. After extraction, a pale yellow powder of HL^b was obtained by evaporation. (6.61 g, yield 67 %) Anal. (calcd.) for $C_{17.4}H_{16.4}N_3O_{0.3}$ ($C_{17}H_{15}N_3O_2 \cdot 0.2C_2H_5OH \cdot 0.1H_2O$): C,68.57 (68.67); H,5.33 (5.43); N,14.07 (13.81) %. 1H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, 2H), 8.26 (d, 2H), 8.11 (d, 2H), 8.04 (t, 1H), 7.71 (s, 1H), 7.60 (t, 1H), 7.53 (t, 2H), 7.28 (s, 1H), 4.54 (q, 2H), 1.51 (t, 3H). FT-IR (KBr, cm^{-1}

¹): 3470 (s, $\nu_{\text{N-H}}$) 1713 (s, $\nu_{\text{C=O}}$)

Synthesis of 6-[5-phenyl-1H-pyrazol-3-yl]-pyridine-2-carboxylic acid (HL^c)

A solution of 2 M NaOH in 100 mL of water was added in a solution of HL^b (3.01 g, 10.3 mmol) in 65 mL ethanol. After addition, the mixture was refluxed at 80 min and evaporated to remove ethanol. The white precipitate was solved in 300 mL H₂O and washed by dichloromethane to remove impurities. After extraction, the water layer was adjusted pH 8 by 12 M HCl, and stir 2 h at room temperature. White solid of HL^c was obtained by filtration and drying. The crude compound was used for synthesis of H₂L. (2.25 g, yield 82 %) Anal. (calcd.) for C₁₅H₁₆N₃O_{4.5} (C₁₅H₁₁N₃O₂·2.5H₂O): C,58.21 (58.06); H,4.80 (5.20); N,13.61 (13.54) %. FT-IR (KBr, cm⁻¹): 3334 (s, $\nu_{\text{N-H}}$) 1701 (s, $\nu_{\text{C=O}}$) ¹H NMR (400 MHz, CDCl₃): δ 7.34 (t, 1H) 7.38 (s,1H) 7.46 (t, 2H) 7.87 (s, 1H) 7.89 (d, 1H) 7.91 (d, 1H) 7.95 (t, 1H) 7.99 (d, 1H). FT-IR (KBr, cm⁻¹): 3334 (s, $\nu_{\text{N-H}}$) 1701 (s, $\nu_{\text{C=O}}$).

Synthesis of 2-[6-[5-(phenyl)-1H-pyrazol-3-yl]-2-pyridinyl]-1H-benzimidazole (H₂L)

HL^c (2.10 g, 7.9 mmol) was added in polyphosphoric acid (25 g) at 180 °C and stirred 15 min. After stirring, o-phenylenediamine (0.854 g, 7.9 mmol) was added and stirred 7 h. The resulting dark green oil was added to water and a pale gray/green suspension was obtained. This mixture was adjusted to pH 10 by using 28 % ammonia solution. A dark beige solid was then obtained by filtration. The filtered solid was then re-dissolved in hot acetone and filtered once more to remove impurities. A beige microcrystalline powder of H₂L was then obtained by evaporation of acetone. (1.68 g, yield 63 %) Anal. (calcd.) for C₂₁H₁₉N₅O₂: C,67.55 (67.85); H,5.13 (5.16); N,18.75 (18.78) %. ¹H NMR (400 MHz, CDCl₃): δ 12.96 (s, 1H), 8.22 (d, 1H), 8.10 (t, 1H), 8.02 (d, 1H), 7.92 (d, 2H), 7.76 (d, 1H), 7.67 (d, 1H), 7.63 (s, 1H), 7.51 (t, 2H), 7.39 (t, 1H), 7.34 (t, 1H), 7.29 (t, 1H). FT-IR (KBr, cm⁻¹): 3201.8 (s, $\nu_{\text{N-H}}$) 1602.9 (s, $\nu_{\text{C-H}}$)

Synthesis of H₂L¹

A beige powder of H₂L¹ was then obtained by evaporation of acetone. (yield 79.2 %) Anal. (calcd.) for H₂L¹ · H₂O (C₂₂H₁₉N₅O): C,71.60 (71.53); H,5.36 (5.18); N,18.88 (18.96) %. ¹H NMR (400 MHz, DMSO): 8.22 (d, 1H), 8.09 (t, 1H), 8.01 (d, 1H), 7.80 (d, 2H), 7.76 (d, 1H), 7.67 (d, 1H), 7.58 (s, 1H), 7.31 (m, 4H), 2.37 (s, 3H). FT-IR (KBr, cm⁻¹): 3142.0 (s, $\nu_{\text{N-H}}$) 1600.9 (s, $\nu_{\text{C-H}}$).

Synthesis of H₂L²

A beige powder of H₂L² was then obtained by evaporation of acetone. (yield 37.0 %) Anal. (calcd.) for H₂L² · 0.5H₂O (C₂₄H₂₂N₅O_{0.5}): C,74.21 (74.20); H,5.65 (5.71); N,18.22 (18.03) %. ¹H NMR (400 MHz, CDCl₃): δ 10.9 (s, 1H), 8.38 (d, 1H), 7.93 (t, 1H), 7.85 (t, 1H), 7.47 (t, 1H), 7.28 (m, 2H), 7.26 (s, 1H), 6.97 (s, 2H), 6.90 (s, 1H), 2.32 (s, 3H), 2.16 (s, 6H).4 FT-IR (KBr, cm⁻¹): 3203.8 (s, $\nu_{\text{N-H}}$) 1604.8 (s, $\nu_{\text{C-H}}$).

Synthesis of H₂L³

A brown powder of H₂L³ was then obtained by evaporation of acetone. (yield 41.2 %) Anal. (calcd.) for (H₂L³ · H₂O · 0.8(CH₃)₂CO) C_{28.4}H_{31.8}N₅O_{1.8}: C,72.18 (72.27); H,6.70 (6.79); N,14.97 (14.84) %. ¹H NMR (400 MHz, DMSO): δ 12.89 (s, 1H), 8.21 (d, 1H), 8.05 (d, 2H), 7.74 (d, 1H), 7.60 (d, 1H), 7.27 (m, 2H), 2.26 (s, 3H), 2.22 (s, 6H). 2.01 (s, 6H), FT-IR (KBr, cm⁻¹): 3172.9 (s, $\nu_{\text{N-H}}$) 1599.0 (s, $\nu_{\text{C-H}}$).

Reference

- [S1] Unpublilshed results (Submitted to *Angew. Chem. Int. Ed.*), T. Shiga, R. Saiki, L. Akiyama, R. Kumai, D. Natke, F. Renz, J.M. Cameron, G.N. Newton and H. Oshio
[S2] T. Shiga, M. Noguchi, T. Matsumoto, H. Sato, H. Tahira, G.N. Newton, H. Oshio, *Pure Appl. Chem.*, **2011**, *83*, 1721–1729.