# **Supporting information**

# Bi-stable spin-crossover in charge-neutral [Fe(R-ptp)<sub>2</sub>] (ptp= 2-(1H-pyrazol-1-yl)-6-(1H-tetrazol-5-yl)pyridine) complexes

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#### **S1. Experimental Section**

#### Instrumentation

### **Photophysical measurements**

UV-Vis absorption spectral measurements were performed with a Varian Cary 5000 double-beam UV-Vis-NIR spectrometer. The ligand and complex were dissolved in 1:1 dichloromethane (DCM), acetonitrile (ACN) solvent mixture. Solution phase PL measurements were performed on a Photon Technology International (PTI) spectrometer at ambient temperature.

#### X-ray crystallography

X-ray diffraction data collection was carried out on a Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N2 device, using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The crystaldetector distance was 36 mm. The cell parameters were determined (Denzo software) from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20s exposure. The structure was solved by direct methods using the program SHELXS-2013.The refinement and all further calculations were carried out using SHELXL-2013. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F2. For complex 5, the atoms O2, C11 and C12 are disordered over two positions with a 0.6/0.4 ratio.

#### **Magnetic measurements**

Magnetic measurements were performed on an MPMS-XL7 SQUID magnetometer (Quantum Design). For standard magnetic measurement in the dark, the temperature-dependent magnetization was recorded at BDC = 1 T (crystalline sample) or 0.1 T (microcrystalline sample) as an external magnetic field. Scan rates of 5, 3, and 1 K min<sup>-1</sup> were employed to study the SCO behavior of the complexes. However, the SCO of the complexes discussed in this study is scan

rate independent. Gelatine capsules (standard measurements in the dark) were used as sample holders in the temperature range of 5 K  $\leftrightarrow$  385 K. The diamagnetic corrections to the molar magnetic susceptibilities were applied using Pascal's constants.

#### **DSC, TGA, and SAXS measurements**

DSC measurements were performed with a TA Instruments DSCQ1000 instrument operated at a scanning rate of 2 °C min<sup>-1</sup> on heating and on cooling. TGA measurements were performed with a TA Instruments Q50 instrument operated at a scanning rate of 5 C min<sup>-1</sup>. SAXS patterns were obtained with a linear monochromatic Cu K $\alpha$ 1 beam ( $\lambda$ = 1.5405 Å) obtained using a sealed-tube generator equipped with a bent quartz monochromator and a curved Inel CPS 120 gas-filled detector; periodicities up to 70 Å can be measured, and the sample temperature-controlled to within ±0.01 °C from 5 °C to 200 °C. The sample was introduced in home-made sealed cells with aluminum windows, and exposure times were varied between 4 and 8 h.

#### S2. Materials and methods

Anhydrous solvents, 1, 10-phenanthroline monohydrate, CuI, Et<sub>3</sub>N, K<sub>2</sub>CO<sub>3</sub>, and Fe(BF<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O were purchased from commercial sources and used as received. Glassware was dried in a vacuum oven at 150 °C prior to the experiments. All the complexation reactions were performed under argon (Ar) atmosphere.

#### **S3.** Computational Details

All H\_elec were extracted from geometry optimizations of isolated molecules, at the PBE+U+D2 level, carried out using Quantum Espresso (QE) version 5.1.1,<sup>1</sup> the PBE functional with a Hubbard-like U parameter of 2.65 eV on the "d" orbitals of iron (PBE+U), the D2 correction of Grimme,<sup>2</sup> and Vanderbilt Ultrasoft pseudopotentials.<sup>3</sup> The use of a DFT-functional including the

parameter U stems from the inability of neither GGA nor hybrid functionals to provide reliable values of  $H_{elec}$ . The former over stabilize the LS state and the latter over stabilize the HS state.<sup>4</sup> This so-called PBE+U+D2 method is especially devised to provide accurate  $\Delta H_{elec}$  values in SCO materials in the gas phase and in the solid-state.<sup>5</sup> The accuracy of this method when dealing with orbital energies is essentially that of PBE, so we have complemented our computational analysis with a more sophisticated DFT functional, the meta-hybrid TPSSh, yielding very similar results concerning the ligand field splitting but poorer  $\Delta H_{elec}$  values (Section S8, table S4 and S5). The evaluation of the transition temperatures  $(T_{1/2})$  has been done accounting for the vibrational contribution to enthalpy  $(H_{vib})$ , and the vibrational and electronic contributions to entropy  $(S_{vib})$ , and Selec, respectively). Hvib has been evaluated following the harmonic-oscillator (HO) approximation. Svib is evaluated using a mixed scheme; frequencies below the cutoff (set at 100 cm<sup>-1</sup>) are treated with the free-rotor approximation and those above are treated with the HO approximation. A damping function is used to avoid discontinuities around the cutoff value. The frequencies were computed with Gaussian 09d at the PBE-D2 level using the QE minima as starting geometry. Finally, Selec can be considered, as a good approximation, to be temperatureindependent with values 13.38 and 0 J·K<sup>-1</sup>·mol<sup>-1</sup> for HS (S=2) and LS (S=0) molecules, respectively.

## S4. Syntheses of ligands and complexes

#### Syntheses of ligands



Scheme S1. Key: (a) EtOH, H<sub>2</sub>SO<sub>4</sub>, Reflux, 12 h, (b) Pyrazole, 1,10-phenanthroline monohydrate, CuI, and K<sub>2</sub>CO<sub>3</sub> in Toluene, 120°C, 2 h; (c) CuCN in DMF, 150°C, under Ar, 2 h; (d) NaN<sub>3</sub>/NH<sub>4</sub>Cl in DMF, 100°C, 20 h.

Synthesis of ethyl 2,6-dibromoisonicotinate (2): To 100 ml of dry EtOH in a 250 mL flask, 2,6dibromoisonicotinic acid (1) (14.05 g, 50 mmol) and 5 ml of H<sub>2</sub>SO<sub>4</sub> were added and the solution was stirred at reflux overnight. After cooling to room temperature, solvents were removed under reduced pressure. The precipitate was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with saturated NaHCO<sub>3</sub> solution followed by water. Crude ester was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as an eluent. Yield: 11 g (71%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (s, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H) ppm.

Synthesis of 2-bromo-6-pyrazol-1-yl-isonicotinic acid ethyl ester (3): To 100 ml of dry and Ar bubbled toluene in a 250 mL two-neck flask, ethyl-2, 6-dibromoisonicotinate (2) (6.16 g, 20 mmol), pyrazole (1.36 g, 20 mmol), 1,10-phenanthroline monohydrate (0.393 g, 2 mmol, 10 mol %), CuI (0.38 g, 2 mmol, 10 mol %) and K<sub>2</sub>CO<sub>3</sub> (3.8 g, 25 mmol) were added and stirred at 120 °C for 2 h. After cooling to room temperature, the mixture was filtered through celite, and the solvent was removed under reduced pressure. Crude ester was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as an eluent. Yield: 3.1 g (52%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.54 (d, *J* = 2.6 Hz, 1H), 8.45 (d, *J* = 0.7 Hz, 1H), 7.90 (d, *J* = 0.7 Hz, 1H), 7.78 (s, 1H), 6.55 – 6.42 (m, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  163.29, 152.03, 143.12, 142.70, 140.45, 127.78, 124.70, 110.78, 108.62, 62.40, 14.19 ppm. ESI-MS in CH<sub>2</sub>Cl<sub>2</sub> (Da): m/z, (assigned structure) = 296.0227 (C<sub>12</sub>H<sub>10</sub>BrN<sub>3</sub>O<sub>2</sub>, [M+H<sup>+</sup>], calc. = 296.00). Elemental Analysis: Calc. for: C<sub>11</sub>H<sub>10</sub>BrN<sub>3</sub>O<sub>2</sub> C, 44.62; H, 3.40; N, 14.19; Found: C, 45.23; H, 3.47; N, 13.98.

#### Synthesis of 2-cyano-6-pyrazol-1-yl-isonicotinic acid ethyl ester (4)

To 5 ml of dry and Ar bubbled DMF, 2-bromo-6-pyrazol-1-yl-isonicotinic acid ethyl ester (**3**) (1.25g, 4.22 mmol) and copper(I)cyanide (0.453g, 5 mmol) were added and the mixture was heated to 150°C under Ar for 2 hrs. DMF was evaporated under reduced pressure, solids were extracted with EtOAc and washed with distilled water and dried over MgSO<sub>4</sub>. Purification of the crude mixture by silica gel chromatography using dichloromethane as an eluent yielded compound **4** as a white solid. Yield: 0.45g (44%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.76 (d, *J* = 1.2 Hz, 1H), 8.58 (d,

J = 2.7 Hz, 1H), 8.10 (d, J = 1.1 Hz, 1H), 7.82 (d, J = 1.3 Hz, 1H), 6.55 (dd, J = 2.6, 1.7 Hz, 1H), 4.55 – 4.40 (m, 2H), 1.46 (t, J = 7.1 Hz, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  179.76, 162.73, 143.54, 142.03, 132.38, 127.82, 124.91, 116.15, 109.27, 62.76, 14.12 ppm. Elemental Analysis: Calc. for: C<sub>12</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>·0.2H<sub>2</sub>O, C, 58.63; H, 4.26; N, 22.79; Found: C, 58.54; H, 4.18; N, 22.40.

#### Synthesis of 2-pyrazol-1-yl-6-(1H-tetrazol-5-yl)-isonicotinic acid ethyl ester (L<sup>4</sup>H)

To 6 ml of dry DMF, 2-cyano-6-pyrazol-1-yl-isonicotinic acid ethyl ester (**4**) (0.485g, 2 mmol), sodium azide (0.192 g, 3 mmol) and ammonium chloride (0.158g, 3 mmol) were added and the mixture heated to 100°C for 20 hrs. Reaction mixture was poured into ice cold water and pH adjusted to 3 using 1N HCl. The precipitate was filtered and washed with water and dried under reduced pressure. The white solid was further washed with dichloromethane and dried under vacuum. Yield: 0.457g (80%). <sup>1</sup>H NMR (300 MHz, DMSO)  $\delta$  9.02 (s, 1H), 8.39 (d, *J* = 1.1 Hz, 2H), 7.94 (s, 1H), 6.72 (d, *J* = 1.7 Hz, 1H), 4.44 (dt, *J* = 7.0, 5.8 Hz, 2H), 1.39 (td, *J* = 7.1, 2.4 Hz, 3H) ppm. <sup>13</sup>C NMR (75 MHz, DMSO)  $\delta$  163.68, 152.14, 143.98, 142.61, 136.25, 128.80, 122.82, 118.53, 113.05, 112.73, 109.65, 106.40, 62.80, 14.43 ppm. ESI-MS in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (Da): m/z, (assigned structure) = 284.09 (C<sub>13</sub>H<sub>11</sub>N<sub>7</sub>O<sub>2</sub>, [M+H<sup>+</sup>], calc. = 284.0824). Elemental Analysis: Calc. for: C<sub>12</sub>H<sub>11</sub>N<sub>7</sub>O<sub>2</sub>·0.5H<sub>2</sub>O, C, 48.98; H, 4.11; N, 33.32; Found: C, 48.85; H, 4.09; N, 32.5.

#### Synthesis of (2-(1H-pyrazol-1-yl)-6-(1H-tetrazol-5-yl)pyridin-4-yl)methanol (L<sup>2</sup>H)

To an ice-cold suspension of L<sup>4</sup>H (0.285g, 1 mmol) in 10 ml of dry EtOH, NaBH<sub>4</sub> (0.078 g, 2 mmol) was added and the reaction mixture was heated to reflux for 12 hrs. The mixture was poured into ice cold water and pH adjusted to 3 using 1N HCl. The precipitate was filtered and washed with water and dried under reduced pressure. Yield: 0.200g (82%). <sup>1</sup>H NMR (300 MHz, DMSO)  $\delta$  9.02 (d, *J* = 2.1 Hz, 1H), 8.05 (s, 2H), 7.87 (s, 1H), 6.66 (s, 1H), 4.74 (s, 2H) ppm. <sup>13</sup>C NMR (75 MHz, DMSO)  $\delta$  158, 154, 151, 143, 142, 128, 117, 110, 109, 62 ppm. ESI-MS in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (Da): m/z, (assigned structure) = 242.0768 (C<sub>11</sub>H<sub>9</sub>N<sub>7</sub>O, [M+H<sup>+</sup>], calc. = 242.08). Elemental Analysis: Calc. for: C<sub>10</sub>H<sub>9</sub>N<sub>7</sub>O·H<sub>2</sub>O, C, 45.98; H, 4.24; N, 37.53; Found: C, 46.03; H, 4.02; N, 36.48.

**Synthesis of 2-Pyrazol-1-yl-6-(1H-tetrazol-5-yl)-isonicotinic acid:** Compound L<sup>4</sup>H (0.542g, 2 mmol) was added to 20 ml of water followed by 85% KOH (0.79g, 12 mmol). The mixture was refluxed overnight and cooled to RT. pH of the solution was adjusted to 2 by adding 1N HCl

solution, A precipitation occurred. The slurry was stirred under RT for a hour, filtered under vacuum and washed with water until pH of the filtrate neutral. The slightly yellowish material was dried under vacuum to obtain the title compound in pure form. **Yield:** 0.403g (78.34%) <sup>1</sup>**H NMR** (300 MHz, d<sup>6</sup>-DMSO, 300 K, TMS):  $\delta$ = 9.015-9.008 (d, J=2.1 Hz, 1H), 8.381 (s, 2H), 7.924 (s, 1H), 6.702 (s, 1H). <sup>13</sup>C NMR (75 MHz, DMSO, 300 K, TMS): 109.009, 112.766, 118.351, 128.252, 143.219, 143.35, 151.644, 154.098, 164.669, ppm. ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH): m/z = 280.055 [M+Na]<sup>+</sup>. Elemental Analysis: Calc. for: **1.5** (C<sub>10</sub>H<sub>7</sub>N<sub>7</sub>O<sub>2</sub>) C, 46.70; H, 2.74; N, 38.12; Found: C, 46.70; H, 2.78; N, 36.50.

Synthesis of 2-Pyrazol-1-yl-6-(1H-tetrazol-5-yl)-isonicotinic acid 4-pyren-1-yl-butyl ester (L<sup>5</sup>H): An oven dried 25 mL Schlenk flask with a stir bar was charged with 2-Pyrazol-1-yl-6-(1H-tetrazol-5-yl)-isonicotinic acid (0.257g, 1mmol) and 4-pyrenebutanol (0.274g, 1 mmol), and the solids placed under Argon atmosphere. To this, anhydrous CH<sub>2</sub>Cl<sub>2</sub> (25 mL) was added and the mixture cooled to 0°C in a Ice-Water bath. DCC (0.206 g, 1mmol) and DMAP (0.122 g, 1mmol) were then added to the stirring mixture slowly as solids. The slowly allowed to attain RT and stirred for 24 h. The reaction mixture was evaporated to dryness under reduced pressure. To the obtained yellowish ppt 20 ml of water was added and pH adjusted to 2 by careful addition of 1N HCl. The ppt obtained was stirred at RT for a hour and filtered at pump. The solids were washed with washed with water until pH of the filtrate neutral. The slightly yellowish material was dried under vacuum. Purification was accomplished by silica gel column chromatography using 9:1 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH as an eluent. A further recrystallization step from CH<sub>2</sub>Cl<sub>2</sub> yielded ligand L<sup>6</sup>H as a pale-yellow microcrystalline solid. Yield: 0.242g (47.17%). <sup>1</sup>H NMR (300 MHz, DMSO, 300 K, **TMS**):  $\delta = 8.84$  (s, 1H), 8.394-7.901 (m, 12H), 6.671 (s, 1H), 4.453 (s, 2H), 1.943 (s, 4H). <sup>13</sup>C NMR (75 MHz, DMSO, 300 K, TMS): 27.710, 27.982, 32.091, 65.632, 108.699, 108.949, 117.724, 123.396, 124.12, 124.214, 124.727, 124.861, 124.927, 126.054, 126.443, 127.269, 127.447, 127.818, 128.076, 129.261, 130.378, 130.843, 136.559, 141.068, 142.893, 150.762, 151.082, 159.896, 164.009. ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH):  $m/z = 536.1762 [M+Na]^+$ . Elemental Analysis: Calc. for: L. 0.83CH<sub>2</sub>Cl<sub>2</sub> (C<sub>30.83</sub>H<sub>24.66</sub>N<sub>7</sub>O<sub>2</sub>) C, 63.4; H, 4.21; N, 16.79; Found: C, 63.44; H, 4.02; N, 16.69.

#### Syntheses of complexes

Synthesis of powder form of  $[Fe(L^1)_2]$  (1): L<sup>1</sup>H (0.225 g, 1 mmol) was added to 40 ml of DCM and 10 ml of MeOH mixture under Ar. To this 150 µL (1 mmol, slight excess) of Et<sub>3</sub>N was added and stirred for 15 mins. To this Fe(BF<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O (0.179g, 0.5 mmol) dissolved in 2 ml of MeOH was added and the mixture was stirred at room temperature for 24 hrs. A yellowish-red precipitate was obtained which was filtered and washed with 2x5ml of MeOH and dried under vacuum to yield 150 mg (68%) of the complex. Elemental Analysis: Calc. for: 1.H<sub>2</sub>O (C<sub>18</sub>H<sub>14</sub>N<sub>14</sub>OFe) C, 43.37; H, 2.83; N, 39.37; Found: C, 42.62; H, 2.88; N, 38.69.

## Synthesis of [Fe(L<sup>2</sup>)<sub>2</sub>] (2)

**Condition 1:**  $L^{2}H$  (0.012g, 0.05 mmol) was added to 21 ml of DCM and 9 ml of MeOH binary solvent mixture under Ar. To this 7 µL (0.05 mmol, slight excess) of Et<sub>3</sub>N was added and stirred for 15 mins. To this Fe(BF<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O (0.09g, 0.025 mmol) dissolved in 0.5 ml of MeOH was added and the mixture stirred at room temperature for 2 hrs. A clear yellow-orange solution was obtained which was filtered and kept for crystallization under ambient conditions. About 3 mg (~12%) of yellow-orange crystals were isolated after of 2-3 weeks, the crystals are not suitable for x-ray structural investigation due to their small size. No further analyses were carried out for this sample.

**Condition 2:**  $L^{2}H$  (0.025 g, 0.1 mmol) was added to 7 ml of DCM and 3 ml of MeOH mixture under Ar. To this 15 µL (0.1 mmol, slight excess) of Et<sub>3</sub>N was added and stirred for 15 mins. To this Fe(BF<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O (0.017g, 0.05 mmol) dissolved in 0.5 ml of MeOH was added and the mixture was stirred at room temperature for 24 hrs. A yellow-orange precipitate was obtained which was filtered and washed with 2x5ml of MeOH and dried under vacuum to yield 17 mg (68%) of the complex. ESI-MS in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (Da): m/z, (assigned structure) = 563.09 (C<sub>20</sub>H<sub>16</sub>N<sub>14</sub>O<sub>2</sub>FeNa, [M+Na<sup>+</sup>], calc. = 563.08). Elemental Analysis of the yellow-orange microcrystalline precipitate: Calc. for: **2**.H<sub>2</sub>O (C<sub>20</sub>H<sub>18</sub>N<sub>14</sub>O<sub>3</sub>Fe) C, 43.01; H, 3.25; N, 35.13; Found: C, 43.62; H, 2.98; N, 36.29. IR(KBr): 3425, 3338, 3085, 2245, 1629, 1571, 1520, 1482, 1424, 1404, 1054, 965, 852, 798 and 771 cm<sup>-1</sup>.

## Synthesis of [Fe(L<sup>4</sup>)<sub>2</sub>] (4)

**Condition 1:**  $L^4H$  (0.0285g, 0.1 mmol) was added to 21 ml of DCM and 9 ml of MeOH binary solvent mixture under Ar. To this 15  $\mu$ L (0.1 mmol) of Et<sub>3</sub>N was added and stirred for 15 mins.

To this  $Fe(BF_4)_{2.}6H_2O$  (0.017g, 0.05 mmol) dissolved in 0.5 ml of MeOH was added and the mixture stirred at room temperature for 2 hrs. A clear red solution was obtained, which was filtered and kept for crystallization under ambient conditions. 13 mg (39%) of dark red crystals suitable for x-ray structural investigation were isolated after of 2-3 weeks. Elemental Analysis of the crystals: Calc. for: 4 (C<sub>24</sub>H<sub>22</sub>N<sub>14</sub>O<sub>4</sub>Fe) C, 46.02; H, 3.54; N, 31.31; Found: C, 45.42; H, 3.02; N, 31.14.

**Condition 2:** L<sup>4</sup>H (0.0285 g, 0.1 mmol) was added to 7 ml of DCM and 3 ml of MeOH binary solvent mixture under Ar. To this 15  $\mu$ L (0.1 mmol) of Et<sub>3</sub>N was added and stirred for 15 mins. To this Fe(BF<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O (0.017g, 0.05 mmol) dissolved in 0.5 ml of MeOH was added and the mixture was stirred at room temperature for 24 hrs. A red precipitate was obtained which was filtered and washed with 2x5ml of MeOH and dried under vacuum to yield 20 mg (60%) of dark red powder. ESI-MS in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (Da): m/z, (assigned structure) = 647.0943 (C<sub>24</sub>H<sub>20</sub>N<sub>14</sub>O<sub>2</sub>FeNa, [M+Na<sup>+</sup>] calc. = 647.1034). Elemental Analysis of the red powder: Calc. for: 4·H<sub>2</sub>O (C<sub>24</sub>H<sub>24</sub>N<sub>14</sub>O<sub>5</sub>Fe) C, 44.73; H, 3.75; N, 30.43; Found: C, 43.72; H, 3.32; N, 29.46. IR(KBr): 3444, 3091, 3019, 1840, 1732, 1557, 1510, 1478, 1444, 1408, 1367, 1295, 1255, 1213, 1145, 1136, 1054, 1008, 906, 858, 764, 531, and 478 cm<sup>-1</sup>.

Synthesis of  $[Fe(L^5)_2]$  (5): Ligand L<sup>5</sup>H (0.0513g, 0.1 mmol) was added to 15 ml of DCM and 5 ml of MeOH mixture under Ar and stirred until complete solubilization of the ligand occurred. To this, 15 µl of Et<sub>3</sub>N was added and stirred for 15 mins. Fe(BF<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O (0.01687g, 0.05 mmol) was added to the above mixture, a deep-red solution was obtained, which was stirred for 24 h. The red precipitate was filtered, washed with methanol and dried under vacuum. Yield: 11mg (20%). ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH): m/z = 1081.3024 [M+H]<sup>+</sup>. Elemental Analysis: Calc. for: 5·H<sub>2</sub>O (C<sub>60</sub>H<sub>46</sub>N<sub>14</sub>O<sub>5</sub>Fe) C, 65.58; H, 4.22; N, 17.84; Found: C, 65.49; H, 4.1; N, 17.85.

Synthesis of  $[Zn(L^3)_2]$  (6): Ligand L<sup>3</sup>H (0.027g, 0.1 mmol) was added to 21 ml of DCM and 9 ml of MeOH mixture under Ar and stirred until complete solubilization of the ligand occurred. To this, 15 µl of Et<sub>3</sub>N was added and stirred for 15 mins. Zn(BF<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O (0.018g, 0.05 mmol) was added to the above mixture, which was stirred for 2 h. The solution was filtered and kept for crystallization under ambient conditions. 16 mg (50%) of colorless crystals suitable for x-ray structural investigation were isolated after of 2-3 weeks. **Elemental Analysis:** Calc. for: **6**·MeOH (C<sub>23</sub>H<sub>20</sub>N<sub>14</sub>O<sub>5</sub>Zn) C, 43.20; H, 3.16; N, 30.75; Found: C, 42.24; H, 2.71; N, 31.03.

#### S5. Photophysical characteristics of the ligands and the complexes

Electronic (UV-Vis) absorption spectra of the ligands— L<sup>2</sup>H, L<sup>4</sup>H, and L<sup>5</sup>H—and complexes **2**, **4**, and **5** were measured in 7:3 DCM/MeOH solvent mixture as depicted in Figures S1(a-b) and S2a. Ligands L<sup>2</sup>H and L<sup>4</sup>H the showed strong  ${}^{1}(\pi \rightarrow \pi)$  absorption bands around 263 nm and 324 nm and 261 and 296 nm, respectively. In pyrene tethered ligand L<sup>5</sup>H, the transitions in the UV region are dominated by pyrene centred  ${}^{1}(\pi \rightarrow \pi)$  transitions. Apart from the intense transitions in the UV region due to the ligands, the complexes also showed parity and spin allowed metal to ligand charge transfer transition  ${}^{1}(MLCT)$  bands at ~450 nm (**2**), ~510 nm (**4**) and ~511 nm (**5**).



**Figure S1.** UV Vis absorption spectra of (a)  $L^2H$  and  $[Fe(L^2)_2]$  (2) and (b)  $L^4H$  and  $[Fe(L^4)_2]$  (4). The experiments were performed in 7:3 DCM/MeOH solvent mixture.

The observed bathochromic shifting of the (i) lower energy transition of L<sup>4</sup>H in comparison with L<sup>2</sup>H and (ii) MLCT transition of **4** and **5** relative to 2 clearly indicate the more stabilized nature of the  $\pi^*$  orbitals corresponding to L<sup>4</sup>H and L<sup>5</sup>H in comparison with L<sup>2</sup>H.

Upon excitation at 340 nm, the ligand L<sup>5</sup>H and complex **5** showed pyrene-based emission in the 350 nm to 500 nm region as shown in figures 2b and c.



**Figure S2.** (a) UV Vis absorption spectra of  $L^5H$  and  $[Fe(L^5)_2]$  (5). Photoluminescence and photoluminescence excitation spectra of (b)  $L^5H$  and (c)  $[Fe(L^5)_2]$  (5). The experiments were performed in 7:3 DCM/MeOH solvent mixture. For PL and PLE measurements, the absorbance of the solutions was maintained around 0.1.

## S6. X-ray structural data of complexes 4, 5 and 6

Formula	C <sub>24</sub> H <sub>20</sub> FeN <sub>14</sub> O <sub>4</sub>	V/Å <sup>3</sup>	2660.45(14)
FW/g.mol <sup>-1</sup>	624.39	Ζ	4
T/K	173(2)	ρ/g.cm <sup>-3</sup>	1.559
Crystal System	Monoclinic	µ/mm <sup>-1</sup>	0.629
Space group	<i>C</i> 2/ <i>c</i>	θ min-max/°	2.149-27.496

Table S1. Crystallographic data of 4<sup>a</sup>

a/Å	14.9960(5)	Reflns collected	20903
b/Å	12.2416(4)	Indep Reflns	3062
c/Å	14.5185(4)	Parameters	200
α/°	90	GOF on F <sup>2</sup>	1.253
β/°	93.432(2)	R1	0.0660
$\gamma/^{\circ}$	90	wR2	0.1666

a CCDC reference number 1839481

Table S2. Crystallographic data of  $5^a$ 

Formula	C <sub>60</sub> H <sub>44</sub> FeN <sub>14</sub> O <sub>4</sub> ·CH <sub>4</sub> O	$V/Å^3$	2946.6(15)
FW/g.mol <sup>-1</sup>	1112.98	Z	2
T/K	173 K	ρ/g.cm <sup>-3</sup>	1.254
Crystal System	Triclinic	µ/mm <sup>-1</sup>	0.316
Space group	P -1	$\theta$ min-max/°	1.417-28.083
a/Å	10.671(3)	Reflns collected	46721
b/Å	14.937(4)	Indep Reflns	14184
c/Å	19.407(6)	Parameters	624
α/°	103.999(5)	GOF on F <sup>2</sup>	0.947
β/°	98.116(6)	R1	0.0860
$\gamma/^{\circ}$	95.146(5)	wR2	0.2373

a CCDC reference number 1407913

Table S3. Crystallographic data of 6<sup>a</sup>

Formula	C22H16N14O4Zn·	V/Å <sup>3</sup>	5380.0(7)
	CH4O		
FW/g.mol <sup>-1</sup>	637.92	Ζ	8
T/K	173	ρ/g.cm <sup>-3</sup>	1.575
Crystal System	Orthorhombic	µ/mm <sup>-1</sup>	0.978
Space group	Pbca	θ min-max/°	1.835-27.951
a/Å	10.9722(8)	Reflns collected	63593
b/Å	22.0874(18)	Indep Reflns	6452

c/Å	22.1996(18)	Parameters	392
α/°	90	GOF on F <sup>2</sup>	1.073
β/°	90	R1	0.0334
γ/°	90	wR2	0.0848

a CCDC reference number 1957514



**Figure S3.** (a) Hydrogen bonding interactions between methanol solvent and tetrazole nitrogen (H5A-N4, d = 2.00(9) Å) in the unit cell of 5 and (b) Unit cell packing pattern of 5 viewed down crystallographic a axis; intermolecular interactions—H24-N12 (Red circle); d = 2.54(7) Å and H33-O3 (Blue circle); d = 2.22(1) Å— are represented with dotted lines. The Green circle highlights  $\pi$ - $\pi$  interaction between the pyrene fragments, leading to the lamellar self-organization described in the main text.



Figure S4. X-ray structure of 6 (CCDC: 1957514).

**S7. Magnetic properties of the complexes** 



Figure S5.  $X_MT$  versus T plot of powder form of 5, the inset shows the X-ray structure of 5.



**Figure S6.** Experimental (red) and Slichter-Drickamer (SD) fitted (black) cooling branch of  $\chi T$  profile of **1** obtained in the second cycle.



**Figure S7.** Experimental (red) and Slichter-Drickamer (SD) (black) fitted cooling branch of  $\chi T$  profile of **2** obtained in the second cycle.



**Figure S8.** Experimental (red) and Slichter-Drickamer (SD) (black) fitted cooling branch of  $\chi T$  profile of **3** obtained in the second cycle.

# **S8.** Optimized Structures, DOS and Molecular Orbitals





**Figure S9.** Optimized structure of the studied compounds in their LS state. Color code: H (rose), C (black), O (red), N (pale blue), Fe (brown).



**Figure S10.** Total Density of States (DOS) and Projected DOS in the *d* orbitals of Fe in the LS-minima computed using PBE+U+D2. The Fermi energy has been set to 0 eV.

## **TPSSH Calculations**

All "TPSSh" calculations have been performed using the meta-hybrid TPSSh functional and a TZVP basis set as implemented in Gaussian 09d. All calculations have been done using the corresponding unrestricted formalism and an SCF convergence threshold of 10<sup>-6</sup>.

**Table S4.** Average values of the structural parameters of the LS and HS states of the gas-phase minima of 1, 2, 3 and 4, electronic enthalpy difference ( $\Delta H_{elec}$ , in kJ/mol) between their LS (S=0) and HS (S=2) spin states minima, and predicted  $T_{1/2}$  (in °K).

	HS		LS			
	$\bar{d}$ (Fe-N) / Å	$\Sigma$ / degree	$\bar{d}$ (Fe-N) / Å	$\Sigma$ / degree	$\Delta H_{elec}$	$T_{1/2}$
1	2.178	162.22	1.949	88.23	56.3	>800
2	2.183	158.46	1.944	88.27	56.2	>800
3	2.174	161.14	1.947	87.99	60.8	>800
4	2.183	163.68	1.941	87.40	60.7	>800

 $\Sigma = \sum_{i=1}^{12} |90 - \alpha_i|$ , where  $\alpha$  are the twelve cis N-Fe-N angles around the Fe atom.

**Table S5.** Average energy of the two sets of 3d-orbitals for compounds 1, 2, 3 and 4, energy difference between them  $\Delta_0$ , electronic enthalpy  $\Delta H_{elec}$ .

		=0, =0	elee		
	1	2	3	4	
t <sub>2g</sub> (in a.u.)	-0.2009	-0.1943	-0.2090	-0.2076	
e <sub>g</sub> (in a.u.)	-0.0334	-0.0273	-0.0398	-0.0385	
$\Delta_0$ (in a.u.)	0.1675	0.1670	0.1691	0.1692	
$\Delta_0$ (in					
kJ/mol)	439.89	438.57	444.09	444.13	
$\Delta H_{elec}$ (in kJ/mol)	56.3	56.2	60.8	60.7	





**Figure S11.** Set of  $t_{2g}$  molecular orbitals for (a) **4** and (b) **2** computed using TPSSh/TZVP. Top orbitals are  $d_{yz}$  (HOMO-2), middle are  $d_{xz}$  (HOMO-1) and bottom are  $d_{xy}$  (HOMO).



**Figure S12.** TGA curves of powder forms of **1**, **2** and **3** showing absence of weight loss from co-crystallized solvent in the thermal stability range, and weight loss from degradation above 250°C (scan rate: 5°C/min).

#### **S9.** References

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