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Supporting Information

Spacer type mediated tunable spin crossover (SCO) characteristics of pyrene decorated 2, 6-bis(pyrazol-1-yl)pyridine (bpp) based Fe(II) molecular spintronic modules

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Experimental Section

Materials and methods: Anhydrous solvents, 1,0-phenanthroline monohydrate, CuI, K₂CO₃, KOH, pyrenebutanol, pyrene butryicacid and $Fe(BF_4)_2 \times 6H_2O$ 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 reactions were performed under argon (Ar) atmosphere.

Instrumentation

X-ray crystallography

X-Ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal-detector distance was 38mm. The cell parameters were determined (APEX2 software)¹ from reflections taken from tree sets of 12 frames, each at 10s exposure. The structure was solved by direct methods using the program SHELXS-2013.² The refinement and all further calculations were carried out using SHELXL-2013.³ 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.

Magnetic measurements

All herein reported magnetic measurements were performed on a MPMS-XL7 or MPMS-XL5 SQUID magnetometers (Quantum Design). For the standard magnetic measurement in the dark, the temperature dependent magnetization was recorded at $B_{DC} = 0.1$ T external magnetic field. The temperature sweeping rate was 2 K min⁻¹ and it was the same for the cooling and heating modes. Gelatine capsules were used as sample holders in the temperature range 5 \leftrightarrow 400 K. The diamagnetic corrections of the molar magnetic susceptibilities were applied using Pascal's constants. For the photomagnetic experiments, the small amount of sample was introduced onto transparent tape and mounted in to the sample holder. The exact weight of samples (ca 0.1 mg) was obtained by weighting and also verified by comparison of thermal $\chi_m T$ vs. *T* curve with that of a more accurately weighed sample of the same compound. After the cooling to 10 K, the sample, now in the low spin state was irradiated ($\lambda = 637$ nm; 10 mW cm⁻²) and the change in magnetisation was followed. When the saturation point had been reached, the light was switched off, the temperature was increased at a rate of 0.3 K min⁻¹, and the magnetisation was measured at 1 K intervals. T_(LIESST) value was determined from the minimum of the $\partial(\chi T)/\partial T$ vs *T* curve for the thermally induced relaxation process.

Photophysical measurements

UV-vis absorption spectral measurements were performed with a Varian Cary 5000 doublebeam UV-vis spectrometer. For solution phase UV-vis measurements the ligand and complex were dissolved in 7:3 dichloromethane (DCM)-methanol (MeOH) binary solvent mixture. For solid state UV-vis measurements, the ligand and complex were kept in between quartz slides and mounted on the sample holder. Solution and solid phase PL measurements were performed on a Photon Technology International (PTI) spectrometer at ambient temperature.

Synthesis of ligands and complexes





n = 4, [Fe(L¹)₂](BF₄)₂

Key: (a) 1,10-phenanthroline, CuI, pyrazole and K_2CO_3 in toluene, 120°C, under Ar, 3d; (b) KOH in water, 24 hrs; (c) pyrenebutanol, DCC and DMAP in DCM, RT, under Ar, 24 hrs and (d) Fe(BF₄)₂×6H₂O in CH₂Cl₂/MeOH, RT, under Ar, 4 hrs.

Synthesis of 2,6-Di-pyrazol-1-yl- isonicotinic acid methyl ester (1): To 50 mL of dry and Ar bubbled toluene in a dry 250 mL two-neck flask, methyl-2, 6-dibromoisonicotinate (5.88 g, 20 mmol), pyrazole (3.4 g, 50 mmol), 1,10-phenanthroline monohydrate (0.768 g, 4 mmol), CuI (0.76 g, 4 mmol) and K₂CO₃ (7.6 g, 50 mmol) were added and stirred at 120 °C for 72 h. After cooling to room temperature, the mixture was filtered through celite, and the solvent was removed under reduced pressure. Crude ester(s) was purified by silica gel column chromatography using CH₂Cl₂ as eluent. **Yield:** 1.54 g (29 %) for the title compound. Monosubstituted ester, 2-Bromo-6-pyrazol-1-yl-isonicotinic acid methyl ester, was obtained in 34 % yield (1.91 g). Characterization data as in Ref. 4.

Synthesis of 2,6-Di-pyrazol-1-yl-isonicotinic acid (2): 2,6-Di-pyrazol-1-yl-isonicotinic acid methyl ester (1.232 g, 5 mmol) was added to 20 mL of water followed by 85% KOH (1.66 g, 30 mmol). The mixture was refluxed overnight and cooled to RT. The pH of the solution was adjusted to 2 by adding 1 N HCl solution leading to a precipitate formation. The slurry was stirred under RT for 1 h, filtered under vacuum and washed with water until pH of the filtrate was neutral. The half white material was dried under vacuum to obtain the title compound in pure form. Yield: 0.920 g (72.1 %). ¹H NMR (300 MHz, DMSO, 300 K, TMS): δ = 14.074 (s, 1H), 8.985-8.978 (d, J = 2.1 Hz, 2 H), 8.156 (s, 2 H), 7.901 (s, 2 H), 6.655 (s, 2 H). ¹³C NMR (75 MHz, DMSO, 300 K, TMS): 107.533, 108.306, 127.843, 142.646, 143.948, 149.846, 164.401 ppm.

Synthesis of 2,6-Di-pyrazol-1-yl-isonicotinic acid 4-pyren-1-yl-butyl ester (L¹): An oven dried 25 mL Schlenk flask with a stir bar was charged with 2 (0.255 g, 1 mmol) and 4-pyrenebutanol (0.274 g, 1 mmol), and the solids placed under argon atmosphere. To this, anhydrous CH₂Cl₂ (20 mL) was added and the mixture cooled to 0°C in an Ice-Water bath. DCC (0.206 g, 1 mmol) and DMAP (0.122 g, 1 mmol) were then added to the stirring mixture slowly as solids and slowly allowed to attain RT and stirred for 72 h. Purification was accomplished by silica gel column chromatography using 9:1 CH₂Cl₂/CH₃OH as an eluent. L¹ was obtained as a half-white powder. Yield: 0.355 g (69 %). ¹H NMR (300 MHz, CDCl₃, 300 K, TMS): $\delta = 8.3$ (m, 3 H), 8.1-7.7 (m, 10 H), 6.5 (s, 2 H), 4.47 (t, 2 H), 3.4 (t, 2 H), 2.1 (m, 4 H) ppm. ¹³C NMR (75 MHz, DMSO, 300 K, TMS): 27.9, 28.6, 33.1, 66.1, 108.5, 109.2, 123.3, 124.8, 124.9, 125.1, 125, 125.9, 126.7, 127, 127.4, 127.48, 127.59, 128.7, 130, 130.9, 131.5, 136, 142.8, 143.4, 150.7, 164.1 ppm. ESI-MS (CH₂Cl₂/CH₃OH): m/z = 534.19 [M+Na]⁺. Elemental Analysis: Calc. for: C₃₂H₂₅N₅O₂×0.4 H₂O: C, 74.09; H, 5.01; N, 13.5; Found: C, 74.14; H, 4.89; N, 13.56.

Synthesis of $[Fe(L^1)_2)](BF_4)_2$: L¹ (0.05157 g, 0.1 mmol) was added to 20 mL of dry DCM under Ar and stirred until complete solubilization of ligand occurred. To this Fe(BF₄)₂×6H₂O (0.0166 g, 0.05 mmol) in 1 mL of MeOH was added. The deep red solution was stirred at RT for 4 hrs. Solvents were evaporated under reduced pressure and the dark red solid was dissolved in minimum amount of acetonitrile and kept for crystallization by slowly diffusing Et₂O. Analytically pure title complex was obtained as microcrystalline solid after 1-2 weeks' time. Yield: 31 mg (49.52 %). ESI-MS (CH₃CN): m/z = 539.1645 [Fe(L¹)₂)]²⁺. Elemental Analysis: Calc.for: C₆₄H₅₀N₁₀O₄FeB₂F₈×H₂O C, 60.5; H, 4.12; N, 11.02; Found: C, 60.57; H, 4.37; N, 11.66. ATR-IR (cm⁻¹): 1720 (v_{C=O}), 1626 (v_{COO}), 1568 (v_{COO}), 1523 (v_{C=C-C}), 1498

 $(v_{C=C-C)}$, 1470 (v_{CH2}) , 1408 (v_{COO}) , 1373 (v_{CN}) , 1134 (v_{CO-O-C}) , 1079 (v_{CO-O-C}) , 1031 (v_{CH}) , 1046 (v_{CH}) , 473 (v_{B-F}) . **UV-vis** $(\lambda_{max}$ (7:3 DCM-MeOH)/nm, $(\epsilon/L^{-1} \text{ cm}^{-1} \text{ mol}^{-1})$): 464 (981), 376 (3190), 343 (107435), 326 (85752), 313 (41833), 276 (120966), 265 (88137), 242 (186624).



Figure S1 Crystal structure of ligand L¹

Table S1 Crystallographic data of L^{1a}

Formula	$C_{32} H_{25} N_5 O_2$	V/Å ³	1238.68(7)
FW/g.mol ⁻¹	511.57	Ζ	2
T/K	173	ρ/g.cm ⁻³	1.372
Crystal System	Triclinic	μ/mm ⁻¹	0.088
Space group	P -1	θ min-max/°	0.965-27.484
a/Å	8.1528(3)	Reflns collected	5672
b/Å	11.4097(4)	Indep Reflns	5647
c/Å	13.9181(4)	Parameters	352
α/°	92.340(2)	GOF on F ²	1.027
β/°	90.367(2)	R1	0.0579
γ/°	106.720(2)	wR2	0.1900

^a CCDC 1441521



Figure S2 UV-vis absorption spectra of L^1 and $[Fe(L^1)_2)](BF_4)_2$ in (top) 7:3 dichloromethane-methanol binary solvent mixture and (bottom) solid state.



Figure S3 Photoluminescence (PL) spectra of L¹ and $[Fe(L^1)_2)](BF_4)_2$ in (top) 7:3 dichloromethane-methanol binary solvent mixture, the optical density of the solutions was kept at ca. 0.1 at the excitation wavelength ($\lambda = 346 \text{ nm}$), and (bottom) solid state ($\lambda = 350 \text{ nm}$). Note the loss of spectral fine structure upon moving from solution to solid phase.

Scheme S2



Key: (a) NaBH₄, 24 hrs; (b) pyrenebutryic acid or pyreneacetic acid, DCC and DMAP in DCM, RT, under Ar, 24 hrs and (c) $Fe(BF_4)_2 \times 6H_2O$ in $CH_2Cl_2/MeOH$, RT, under Ar, 4 hrs.

Synthesis of (2,6-Di-pyrazol-1-yl-pyridin-4-yl)-methanol (2): The title compound was synthesized according to the literature procedure from **1.**⁵

Synthesis of 5-Pyren-1-yl-pentanoic acid 2, 6-di-pyrazol-1-yl-pyridin-4-ylmethyl ester (L²): An oven dried 25 mL Schlenk flask with a stir bar was charged with 2 (0.241 g, 1 mmol) and pyrenebutyricbutryic acid (0.288 g, 1 mmol), and the solids placed under Argon atmosphere. To this, anhydrous CH₂Cl₂ (20 mL) was added and the mixture cooled to 0°C in an Ice-Water bath. DCC (0.206 g, 1 mmol) and DMAP (0.122 g, 1mmol) were then added to the stirring mixture slowly as solids and allowed to attain RT and stirred for 72 h. Purification was accomplished by silica gel column chromatography using CH₂Cl₂ as an eluent and the product was recrystallized from hexane to yield L² as white powder in analytically pure form. **Yield:** 0.353 g (69 %). ¹H NMR (300 MHz, CDCl₃, 300 K, TMS): $\delta = 8.54$ (d, 2 H), 8.3 (d, 1 H), 8.1 (m, 8 H), 7.76 (s, 2 H), 7.75 (d, 2 H), 6.5 (q, 2 H), 5.15 (s, 2 H), 3.5 (t, 2 H), 2.6 (t, 2 H), 2.3 (p, 2 H) ppm. ¹³C NMR (75 MHz, DMSO, 300 K, TMS): 26.8, 33, 34, 64, 107, 108, 123, 124.9, 125, 125.9, 126.9, 127.3, 127. 6, 128.9, 130.2, 131, 131.5, 135.6, 142.6, 150.5, 151.4, 173.1 ppm. **ESI-MS (CH₂Cl₂/CH₃OH):** m/z = 534.19 [M+Na]⁺. **Elemental Analysis:** Calc. for: C₃₂H₂₅N₅O₂×0.4 H₂O: C, 74.09; H, 5.01; N, 13.5; Found: C, 74.03; H, 4.91; N, 13.52.

Synthesis of $[Fe(L^2)_2)](BF_4)_2$: L² (0.102 g, 0.2 mmol) was added to 20 mL of dry DCM under Ar and stirred until complete solubilization of ligand occured. To this Fe(BF₄)₂×6H₂O (0.034 g, 0.1 mmol) in 1 mL of MeOH was added. The yellow solution was stirred at RT for 4 hrs. Solvents were evaporated under reduced pressure and the solid was dissolved in minimum amount of acetonitrile and kept for crystallization by slowly diffusing Et₂O. Analytically pure title complex was obtained as microcrystalline solid after 1-2 weeks' time. **Yield:** 66 mg (53 %). **ESI-MS (CH₃CN):** m/z = 539.17 [**Fe(L²)**₂)]²⁺. **Elemental Analysis:** Calc.for: C₆₄H₅₀N₁₀O₄FeB₂F₈×H₂O C, 60.5; H, 4.12; N, 11.02; Found: C, 60.47; H, 4.25; N, 11.24. **ATR-IR (**cm⁻¹)**:** 1743 (v_{C=O)}, 1634 (v_{COO}), 1576 (v_{COO}), 1522 (v_{C=C-C}), 1462 (v_{CH2}), 1406 (v_{COO}), 1334 (v_{CN}), 1174 (v_{CO-O-C}), 1049 (v_{CO-O-C}), 485 (v_{B-F}). **UV-vis** (λ_{max} (7:3 DCM-MeOH)/nm, (ϵ /L⁻¹ cm⁻¹ mol⁻¹)): 425 (968), 376 (2955), 343 (88401), 326 (73970), 312 (57733), 275 (115587), 265 (92428), 242 (153387).



Figure S4 UV-vis absorption spectra of L^2 and $[Fe(L^2)_2)](BF_4)_2$ in (top) 7:3 dichloromethane-methanol binary solvent mixture and (bottom) solid state.



Figure S5 Photoluminescence (PL) spectra of L^2 and $[Fe(L^2)_2)](BF_4)_2$ in (top) 7:3 dichloromethane-methanol binary solvent mixture, the optical density of the solution was kept at ca. 0.1 at the excitation wavelength ($\lambda = 346 \text{ nm}$), and (bottom) solid state ($\lambda = 350 \text{ nm}$). Note the loss of spectral fine structure upon moving from solution to solid phase.

References

- 1. "M86-E01078 APEX2 User Manual", Bruker AXS Inc., Madison, USA, 2006.
- 2. G. M. Sheldrick, Acta Cryst. 1990, A46, 467-473.
- 3. G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.
- 4. R. Chandrasekar, F. Schramm, S. Brink, O. Fuhr, M. Ghafari, R. Kruk and M. Ruben, *Inorg. Chem.* 2006, **45**, 10019–10021.
- 5. J. Elhaik, C. M. Pask, C. A. Kilner and M. A. Halcrow, *Tetrahedron*, 2007, 63, 291–298.