Defying the inverse energy gap law: a vacuum-evaporable Fe(II) low-spin complex with a long-lived LIESST state

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S1 Experimental

S1.1 General synthetic procedures

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques or in an M. Braun LabMaster 130 glovebox under argon, unless stated otherwise. Chemicals were purchased from commercial sources and used without further purification. Solvents were purchased from commercial sources, purified by distilling under N_2 or Ar atmosphere over conventional drying agents and freshly distilled prior to use. Solvent evaporation was performed at 45 °C at appropriate pressure. Solvent residues were removed under a high vacuum.

S1.1.1 Column chromatography.

Flash column chromatography was performed using a Biotage Isolera One Flash Chromatography System with prepacked columns of the types SNAP Ultra (spheric silica) or CHROMABOND Flash BT25 SiOH. All solid crude products were dry-loaded by adding about 4 g of silica (more or less if necessary) prior to removing the solvent in vacuo.

S1.1.2 Product characterization.

NMR spectra were recorded in deuterated solvents on a Bruker Avance 400 Pulse Fourier Transform spectrometer operating at a ¹H frequency of 400.1 MHz and a ¹³C frequency of 100.6 MHz. They were referenced to the residual protonated solvent signal (¹H: δ (CHCl₃) = 7.26 ppm; δ (DMSO-d₆) = 2.50 ppm), the solvent signal (¹³C: δ (CDCl₃) = 77.16 ppm; δ (DMSO-d₆) = 39.52 ppm). Signals were assigned with the help of DEPT-135 and two-dimensional correlation spectra (¹H,¹H-COSY, ¹H,¹³C-HSQC, ¹H,¹³C-HMBC). Signal multiplicities in ¹H spectra are abbreviated as s (singlet), d (doublet), t (triplet) and m (multiplet). In ¹³C spectra, the abbreviations s (quaternary), d (tertiary), t (secondary) and q (primary) denote the number of bound hydrogen atoms. Infrared spectra were recorded at room temperature on a Bruker Vertex70 FT-IR spectrometer using a broadband spectral range extension VERTEX FM for full mid and far IR in the range of 6.000-80 cm⁻¹ with a resolution of 3 cm⁻¹. Raman spectra were recorded at room temperature on a Bruker RAM II FT-Raman spectrometer using a liquid-nitrogen-cooled, highly sensitive Ge detector (D418-T/R), 1064 nm radiation (Nd:YAG-laser, up to 500 mW)and 3 cm⁻¹ resolution. Signal intensities are marked as s (strong), m (medium) and w (weak) and may be modified by the prefix v (very ...). Elemental analyses were performed using a vario MICRO cube elemental analyser from Elementar. Samples were burned in sealed tin containers in a stream of oxygen. High-resolution ESI mass spectra were recorded using a Thermo Scientific Q-Exactive Plus in ultimate resolution 280.000.

S1.2 Syntheses

S1.2.1 Synthesis of *N-tert*-butyloxycarbonyl-pyrrole.

This compound was synthesised similarly to a procedure from the literature.¹

At first, 17.2 g di-*tert*-butyl dicarbonate (Boc₂O, 79.0 mmol, 1.2 eq.) and 1.71 g 4-(dimethylamino)pyridine (DMAP, 14.0 mmol, 0.2 eq.) were frozen with liquid nitrogen and the atmosphere exchanged with N₂. At room temperature, 50 mL MeCN and 4.31 g freshly distilled (60 °C, 20 mbar) pyrrole (64.4 mmol, 1 eq.) were added and the resulting yellow solution was stirred in the dark for 64 h. Afterwards, the solution was added to 50 mL of Et₂O and rinsed with a further 50 mL. The organic phase was washed with sat. NH₄Cl-solution, H₂O, sat. NaHCO₃-solution and H₂O (50 mL each), dried over MgSO₄, filtrated, rinsed twice with 25 mL each and the solvent removed *in vacuo*. The product was purified by distillation (125 °C, 20 mbar) and thus obtained as a colourless liquid in a yield of 9.68 g (57.9 mmol, 90 %).

 R_{f} (Cy/DCM 3:1) = 0.31.

IR (ATR): $\tilde{v} = 3152$ (w), 3109 (w), 2980 (w), 2934 (w), 2655 (w), 1740 (s), 1472 (m), 1457 (m), 1400 (m), 1370 (m), 1339 (s), 1314 (s), 1255 (m), 1213 (w), 1195 (m), 1151 (s), 1076 (s), 1032 (m), 951 (s), 926 (w), 868 (w), 851 (m), 826 (w), 772 (m), 736 (s), 590 (m), 538 (w) cm⁻¹.

FT-Raman (KBr): $\tilde{v} = 3157$ (w), 3122 (w), 2985 (m), 2935 (s), 1747 (m), 1473 (s), 1453 (m), 1402 (s), 1345 (m), 1320 (m), 1244 (w), 1197 (w), 1081 (m), 1034 (m), 953 (m), 926 (w), 870 (w), 824 (w), 828 (w), 757 (s) cm⁻¹.

¹**H NMR** (400 MHz, CDCl₃): $\delta = 7.24$ (m, 2 H, H_{pvr}), 6.22 (dd, ${}^{3}J = 2.6$ Hz, ${}^{4}J = 2.1$ Hz, 2 H, H_{pvr}), 1.60 (s, 9 H, C(CH₃)₃) ppm.

¹³**C** NMR (101 MHz, CDCl_3): δ = 149.07 (s, 1 C, *C*=O), 120.10 (d, 2 C, *C*_{pyr}), 111.95 (d, 2 C, *C*_{pyr}), 83.69 (s, 1 C, *C*(CH₃)₃), 28.14 (q, 3 C, C(CH₃)₃) ppm.

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S1.2.2 Synthesis of 6-bromo-2-(pyridine-2'-yl)pyridine.



At first, this compound was synthesised following a procedure from the literature in three steps.² Later on, the following modified one-step synthesis was found to be quicker and easier.^{3,4}

Under N₂ atmosphere (freeze-pump-thaw) and at 0 °C, 5 mL of a 2 M solution of isopropylmagnesium chloride (100 mmol, 1.1 eq.) were added to 1.43 g of 2-bromopyridine (9.02 mmol, 1 eq.). After 4 h of slow warming to room temperature, the brown suspension was cooled again to 0 °C and a solution of 1.47 g of zinc chloride (10.8 mmol, 1.2 eq.) in 6 mL abs. THF was added and rinsed with a further 2 mL. The yellow-brown solution turned into a suspension within 1 h of stirring at room temperature. Afterwards, the suspension was added to 2.14 g 2,6-dibromopyridine (9.03 mmol, 1 eq.) and 320 mg [Pd(PPh₃)₄] at 0 °C, stirred for 30 min and then refluxed (85 °C) for 17 h. The faint yellow suspension was added to 50 mL 0.1 M Na₂EDTA-solution, rinsed twice with 25 mL each and stirred for 4.5 h. The aqueous phase was extracted four times with 35 mL CHCl₃ each, the organic phase dried over MgSO₄, filtrated, rinsed twice with 20 mL each and the solvent removed *in vacuo*. The product was purified by flash column chromatography (silica, cyclohexane + ethyl acetate 6 % \rightarrow 27 %) and thus obtained as a colourless powder in a yield of 1.06 g (4.51 mmol, 50 %).

After the purification, some mixed fractions were received that increased the yield to up to 66 %. While they did include some minor yellow impurities, oftentimes they were used for the next step, nonetheless.

 $\mathbf{R}_{\mathbf{f}}$ (Cy/EtOAc 3:1) = 0.22 (impurities prior to purification at 0.57, 0.35, 0.11 and 0).

Anal. Calcd for C₁₀H₇BrN₂: C, 51.09 %; H, 3.00 %; N, 11.92 %. Found: C, 51.29 %; H, 2.98 %; N, 11.62 %.

IR (ATR): $\tilde{v} = 3093$ (vw), 3059 (w), 3045 (w), 3026 (vw), 3003 (w), 1657 (w), 1614 (vw), 1600 (vw), 1578 (s), 1542 (s), 1476 (w), 1464 (w), 1440 (w), 1420 (s), 1397 (s), 1306 (m), 1258 (m), 1231 (w), 1209 (w), 1151 (m), 1121 (s), 1093 (m), 1066 (s), 1038 (s), 1026 (m), 985 (s), 958 (w), 917 (vw), 902 (w), 889 (w), 807 (w), 790 (m), 764 (s), 744 (s), 681 (s), 630 (m), 618 (m), 605 (m), 586 (w) cm⁻¹.

FT-Raman (KBr): $\tilde{v} = 3094$ (w), 3066 (w), 3028 (vw), 3008 (vw), 1614 (w), 1590 (s), 1570 (s), 1549 (w), 1478 (m), 1444 (m), 1423 (w), 1400 (w), 1311 (m), 1286 (m), 1257 (vw), 1233 (m), 1162 (w), 1153 (vw), 1125 (w), 1094 (w), 1077 (w), 1070 (w), 1042 (m), 995 (s), 986 (m), 813 (w), 794 (w), 780 (vw), 748 (vw), 683 (m), 631 (w), 619 (w), 603 (vw) cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.66 (ddd, ${}^{3}J_{6'.5'}$ = 4.8 Hz, ${}^{4}J_{6'.4'}$ = 1.8 Hz, ${}^{5}J_{6'.3'}$ = 0.9 Hz, 1 H, *H*-6'), 8.42–8.39 (m, 1 H, *H*-3'), 8.38 (dd, ${}^{3}J_{5.4}$ = 7.7 Hz, ${}^{4}J_{5.3}$ = 0.9 Hz, 1 H, *H*-5), 7.82 (ddd, ${}^{3}J_{4'.3'}$ = 8.0 Hz, ${}^{3}J_{4'.5'}$ = 7.5 Hz, ${}^{4}J_{4'.6'}$ = 1.8 Hz, 1 H, *H*-4'), 7.67 (t, ${}^{3}J_{4.3/5}$ = 7.8 Hz, 1 H, *H*-4), 7.49 (dd, ${}^{3}J_{3.4}$ = 7.8 Hz, ${}^{4}J_{3.5}$ = 0.9 Hz, 1 H, *H*-3), 7.32 (ddd, ${}^{3}J_{5'.4'}$ = 7.5 Hz, ${}^{3}J_{5'.6'}$ = 4.8 Hz, ${}^{4}J_{5'.3'}$ = 1.2 Hz, 1 H, *H*-5') ppm.

¹³**C** NMR (101 MHz, CDCl₃): δ = 157.49 (s, 1 C, *C*-2), 154.64 (s, 1 C, *C*-2'), 149.36 (d, 1 C, *C*-6'), 141.73 (s, 1 C, *C*-6), 139.35 (d, 1 C, *C*-4), 137.15 (d, 1 C, *C*-4'), 128.12 (d, 1 C, *C*-3), 124.40 (d, 1 C, *C*-5'), 121.63 (d, 1 C, *C*-3'), 119.85 (d, 1 C, *C*-5) ppm.

S1.2.3 Synthesis of 6-(*N-tert*-butyloxycarbonyl-pyrrole-2-yl)-2-(pyridine-2'-yl)pyridine.



This compound was synthesised following a procedure from the literature.²

Under N₂ atmosphere (freeze-pump-thaw) and cooling with acetone + N_{2(l)}, 2.3 mL *n*-BuLi (2.5 M in *n*-hexane, 5.8 mmol, 1.4 eq.) were added to 567 mg *N*,*N*'-diisopropylamine (5.60 mmol, 1.4 eq.) in 8 mL abs. THF. After 80 min, a solution of 874 mg *N*-tert-butyloxycarbonyl-pyrrole (5.23 mmol, 1.3 eq.) in 4 mL abs. THF was added and rinsed with a further 4 mL. The colourless solution was stirred for a further 60 min at -94 °C before it was quenched with 790 mg trimethyl borate (7.60 mmol, 1.9 eq.) and the resulting colourless solution was stirred for 2 h at 0 °C. Under air, 225 mg [PdCl₂(PPh₃)₂] (321 µmol, 0.08 eq.), 941 mg 6-bromo-2-(pyridine-2'-yl)pyridine (4.00 mmol, 1 eq.) and a solution of 1.11 g K₂CO₃ (8.03 mmol, 2 eq.) in 8 mL deion. H₂O were added and the biphasic mixture refluxed for 16 h, upon which the yellow organic phase turned dark brown. Afterwards, 30 mL Et₂O were added, the mixture was transferred into a separation funnel and rinsed with a further 30 mL. The organic phase was washed three times with 30 mL sat.

NaCl-solution, the aqueous phase extracted twice with 30 mL Et_2O each, the combined organic phase dried over MgSO₄, filtrated, rinsed twice with 20 mL each and the solvent removed *in vacuo*. The product was purified by flash column chromatography (silica, cyclohexane + ethyl acetate 6 % \rightarrow 50 %) and thus obtained as a yellow highly viscous liquid in a yield of 1.19 g (3.70 mmol, 93 %).

 $\mathbf{R}_{\mathbf{f}}$ (Cy/EtOAc 3:1) = 0.19 (impurities prior to purification at 0.53 and 0).

Anal. Calcd for C₁₉H₁₉N₃O₂: C, 71.01 %; H, 5.96 %; N, 13.07 %. Found: C, 70.66 %; H, 6.37 %; N, 12.85 %.

IR (ATR): $\tilde{v} = 3151$ (vw), 3062 (vw), 3007 (w), 2980 (w), 2932 (w), 1737 (s), 1594 (m), 1581 (m), 1568 (s), 1554 (m), 1476 (m), 1448 (s), 1428 (s), 1404 (w), 1392 (m), 1370 (s), 1345 (m), 1313 (vs), 1297 (s), 1255 (m), 1186 (w), 1145 (vs), 1094 (m), 1074 (m), 1048 (m), 1041 (m), 996 (m), 986 (m), 887 (w), 844 (s), 818 (m), 795 (w), 779 (s), 745 (m), 729 (s), 676 (m), 632 (m), 618 (m), 596 (m), 557 (w) cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.68 \text{ (ddd, } {}^{3}J_{6'-5'} = 4.8 \text{ Hz}, \, {}^{4}J_{6'-4'} = 1.8 \text{ Hz}, \, {}^{5}J_{6'-3'} = 0.9 \text{ Hz}, 1 \text{ H}, H_{py}-6')$, 8.46 (ddd, ${}^{3}J_{3'-4'} = 8.0 \text{ Hz}, \, {}^{4}J_{3'-5'} = 1.2 \text{ Hz}, \, {}^{5}J_{3'-6'} = 0.9 \text{ Hz}, 1 \text{ H}, H_{py}-3')$, 8.35 (dd, ${}^{3}J_{3-4} = 7.9 \text{ Hz}, \, {}^{4}J_{3-5} = 1.0 \text{ Hz}, 1 \text{ H}, H_{py}-3)$, 7.82 (t, ${}^{3}J_{4-3/5} = 7.8 \text{ Hz}, 1 \text{ H}, H_{py}-4)$, 7.77 (ddd, ${}^{3}J_{4'-3'} = 8.0 \text{ Hz}, \, {}^{3}J_{4'-5'} = 7.5 \text{ Hz}, \, {}^{4}J_{4'-6'} = 1.8 \text{ Hz}, 1 \text{ H}, H_{py}-4')$, 7.43 (dd, ${}^{3}J_{5-4} = 7.7 \text{ Hz}, \, {}^{4}J_{5-3} = 1.0 \text{ Hz}, 1 \text{ H}, H_{py}-5)$, 7.40 (dd, ${}^{3}J_{5-4} = 3.2 \text{ Hz}, \, {}^{4}J_{5-3} = 1.7 \text{ Hz}, 1 \text{ H}, H_{py}-5)$, 7.29 (ddd, ${}^{3}J_{5'-4'} = 7.5 \text{ Hz}, \, {}^{3}J_{5'-6'} = 4.8 \text{ Hz}, \, {}^{4}J_{5'-3'} = 1.2 \text{ Hz}, 1 \text{ H}, H_{py}-5')$, 6.48 (dd, ${}^{3}J_{3-4} = 3.3 \text{ Hz}, 1 \text{ H}, H_{py}-3)$, 6.27 (t, ${}^{3}J_{4-3/5} = 3.3 \text{ Hz}, 1 \text{ H}, H_{py}-4)$, 1.29 (s, 9 H, C(CH₃) ppm.

¹³**C** NMR (101 MHz, CDCl₃): δ = 156.11 (s, 1 C, *C*_{py}-2'), 155.09 (s, 1 C, *C*_{py}-2), 152.35 (s, 1 C, *C*_{py}-6), 149.46 (s, 1 C, *C*=O), 149.06 (d, 1 C, *C*_{py}-2'), 136.96 (d, 1 C, *C*_{py}-4'), 136.93 (d, 1 C, *C*_{py}-4), 134.45 (s, 1 C, *C*_{py}-2), 123.84 (d, 1 C, *C*_{py}-5'), 123.82 (d, 1 C, *C*_{py}-5), 123.32 (d, 1 C, *C*_{py}-5), 121.53 (d, 1 C, *C*_{py}-3'), 119.06 (d, 1 C, *C*_{py}-3), 115.80 (d, 1 C, *C*_{py}-3), 110.65 (d, 1 C, *C*_{py}-4), 83.71 (s, 1 C, *C*(CH₃)₃), 27.67 (q, 3 C, C(CH₃)₃) ppm.

S1.2.4 Synthesis of 6-(pyrrole-2-yl)-2-(pyridine-2'-yl)pyridine (pypypyrH).



This compound was synthesised following loosely a procedure from the literature.²

Under ambient atmosphere, 100 mL deion. H_2O were added to 1.19 g 6-(*N*-tert-butyloxycarbonyl-pyrrole-2-yl)-2-(pyridine-2'yl)pyridine (3.70 mmol). Afterwards, 8.5 mL 37 % HCl (ca. 100 mmol) were added and rinsed twice with 20 mL H_2O each, upon which the starting material dissolved and turned the solution yellow. After 66 h of stirring at room temperature, the yellow suspension was transferred to a beaker with 60 mL CHCl₃ and alkalised (pH = 8) with 60 mL sat. NaHCO₃-solution, resulting in a yellow-brown organic phase and a milky white aqueous phase. The aqueous phase was extracted three times with 30 mL CHCl₃ each, the combined organic phase dried over MgSO₄, filtrated, rinsed twice with 20 mL each and the solvent removed *in vacuo*. The product was purified by flash column chromatography (silica, cyclohexane + ethyl acetate 4 % \rightarrow 34 %) and thus obtained as a colourless solid in a yield of 694 mg (3.14 mmol, 85 %).

This compound turns yellow-brown over time. Therefore, it was purified freshly prior to further use.

 $\mathbf{R}_{\mathbf{f}}$ (Cy/EtOAc 5:1) = 0.11 (impurities prior to purification at 0.21 and 0).

Anal. Calcd for C₁₄H₁₁N₃: C, 76.00 %; H, 5.01 %; N, 18.99 %. Found: C, 76.04 %; H, 4.92 %; N, 18.99 %.

IR (ATR): $\tilde{v} = 3398$ (m), 3116 (w), 3050 (w), 3007 (w), 1593 (w), 1581 (m), 1565 (m), 1553 (m), 1462 (m), 1451 (m), 1431 (m), 1410 (m), 1327 (w), 1290 (w), 1263 (w), 1251 (w), 1237 (w), 1220 (w), 1178 (w), 1158 (w), 1149 (m), 1114 (m), 1101 (m), 1076 (m), 1053 (m), 1035 (m), 989 (m), 962 (w), 937 (w), 905 (w), 882 (m), 860 (w), 823 (w), 804 (w), 774 (s), 745 (m), 732 (m), 721 (s), 682 (m), 651 (m), 641 (m), 633 (s), 612 (m), 594 (m), 580 (s) cm⁻¹.

FT-Raman (KBr): $\tilde{v} = 3134$ (w), 3116 (w), 3098 (w), 3089 (w), 3077 (w), 3068 (w), 3057 (w), 3048 (w), 3011 (w), 1626 (w), 1616 (w), 1596 (s), 1585 (s), 1568 (s), 1560 (m), 1477 (m), 1465 (s), 1455 (m), 1435 (m), 1416 (m), 1411 (m), 1384 (w), 1331 (m), 1295 (w), 1287 (w), 1267 (w), 1237 (m), 1223 (w), 1151 (w), 1136 (w), 1115 (w), 1103 (w), 1095 (w), 1089 (w), 1064 (w), 1042 (w), 996 (s), 990 (s), 941 (w), 882 (w), 861 (vw), 826 (vw), 801 (w), 795 (w), 781 (vw), 731 (vw), 691 (vw), 683 (w), 636 (w), 620 (w), 583 (vw), 522 (vw) cm⁻¹.

¹**H NMR** (400 MHz, CDCl_3): $\delta = 9.74$ (s, 1 H, $N_{\text{pyr}}H$), 8.70 (ddd, ${}^{3}J_{6'-5'} = 4.8$ Hz, ${}^{4}J_{6'-4'} = 1.8$ Hz, ${}^{5}J_{6'-3'} = 0.9$ Hz, 1 H, H_{py} -6'), 8.48–8.44 (m, 1 H, H_{py} -3'), 8.16 (dd, ${}^{3}J_{3.4} = 7.8$ Hz, ${}^{4}J_{3.5} = 1.0$ Hz, 1 H, H_{py} -3), 7.82 (ddd, ${}^{3}J_{4'-3'} = 8.0$ Hz, ${}^{3}J_{4'-5'} = 7.5$ Hz,

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 ${}^{4}J_{4'-6'} = 1.8$ Hz, 1 H, H_{py} -4'), 7.76 (t, ${}^{3}J_{4\cdot3/5} = 7.8$ Hz, 1 H, H_{py} -4), 7.57 (dd, ${}^{3}J_{5\cdot4} = 7.9$ Hz, ${}^{4}J_{5\cdot3} = 1.0$ Hz, 1 H, H_{py} -5), 7.31 (ddd, ${}^{3}J_{5'-4'} = 7.5$ Hz, ${}^{3}J_{5'-6'} = 4.8$ Hz, ${}^{4}J_{5'\cdot3'} = 1.2$ Hz, 1 H, H_{py} -5'), 6.95 (td, J = 2.6 Hz, ${}^{4}J = 1.4$ Hz, 1 H, H_{pyr} -3), 6.77 (ddd, J = 3.8 Hz, J = 2.5 Hz, ${}^{4}J = 1.4$ Hz, 1 H, H_{pyr} -5), 6.34 (dt, J = 3.6 Hz, J = 2.7 Hz, 1 H, H_{pyr} -4) ppm.

¹³C NMR (101 MHz, CDCl₃): δ = 156.35 (s, 1 C, *C*_{py}-2'), 155.16 (s, 1 C, *C*_{py}-2), 150.03 (s, 1 C, *C*_{py}-6), 149.27 (d, 1 C, *C*_{py}-6'), 137.58 (d, 1 C, *C*_{py}-4), 136.86 (d, 1 C, *C*_{py}-4'), 131.75 (s, 1 C, *C*_{py}-2), 123.77 (d, 1 C, *C*_{py}-5'), 121.11 (d, 1 C, *C*_{py}-3'), 119.82 (d, 1 C, *C*_{pyr}-3), 118.34 (d, 1 C, *C*_{py}-5), 118.06 (d, 1 C, *C*^{py}-3), 110.49 (d, 1 C, *C*_{pyr}-4), 107.44 (d, 1 C, *C*_{pyr}-5) ppm.

S1.2.5 Synthesis of [Zn(pypypyr)₂].



Under N₂ atmosphere, 224 mg 6-(pyrrole-2-yl)-2-(pyridine-2'-yl)pyridine (1.01 mmol, 2 eq.) were dissolved in 10 mL abs. Et₂O. At -94 °C (acetone + N_{2(l)}), 0.5 mL diethylzinc(II) ([Zn(Et)₂], 1 M solution in *n*-heptane, 0.5 mmol, 1 eq.) were added, leading to a yellow suspension. After 30 min, the cooling bath was removed and the suspension slowly warmed to room temperature over 90 min. The now orange suspension was filtrated, the solid residue washed twice with 5 mL abs. Et₂O each, dried *in vacuo* and the product thus obtained as an orange powder in a yield of 209 mg (413 µmol, 83 %).

Anal. Calcd for C₂₈H₂₀N₆Zn: C, 66.48 %; H, 3.99 %; N, 16.61 %. Found: C, 66.50 %; H, 4.08 %; N, 16.37 %.

IR (ATR): $\tilde{v} = 3080$ (vw), 3054 (w), 3012 (vw), 1628 (vw), 1601 (m), 1590 (s), 1569 (w), 1553 (s), 1512 (s), 1474 (m), 1456 (m), 1434 (s), 1390 (m), 1381 (s), 1336 (m), 1310 (m), 1287 (m), 1267 (m), 1250 (m), 1218 (vw), 1193 (w), 1163 (s), 1152 (s), 1144 (s), 1114 (w), 1082 (w), 1059 (m), 1030 (s), 1010 (m), 999 (s), 977 (m), 942 (s), 896 (w), 884 (w), 874 (w), 855 (w), 842 (w), 815 (w), 799 (m), 772 (s), 749 (m), 738 (s), 726 (s), 718 (s), 695 (m), 681 (s), 656 (m), 624 (m), 611 (m), 536 (w) cm⁻¹.

FT-Raman (KBr): $\tilde{v} = 3107$ (vw), 3080 (vw), 3058 (w), 1602 (m), 1592 (s), 1571 (w), 1556 (s), 1516 (s), 1477 (m), 1459 (w), 1440 (w), 1385 (vs), 1340 (m), 1313 (w), 1292 (m), 1270 (w), 1256 (w), 1196 (w), 1168 (w), 1149 (w), 1114 (w), 1090 (w), 1060 (m), 1039 (w), 1031 (w), 1012 (s), 1003 (m), 989 (w), 978 (vw), 944 (w), 896 (w), 876 (vw), 819 (vw), 800 (w), 770 (vw), 756 (vw), 731 (vw), 685 (w), 657 (w), 626 (vw), 537 (vw) cm⁻¹.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.34$ (dt, ${}^{3}J_{3'.4'} = 8.1$ Hz, ${}^{4}J_{3'.5'} = 1.0$ Hz, ${}^{5}J_{3'.6'} = 1.0$ Hz, 2 H, H_{py} -3'), 8.03 (t, ${}^{3}J_{4.3} = 7.6$ Hz, ${}^{3}J_{4.5} = 7.6$ Hz, 2 H, H_{py} -4'), 7.99 (dd, ${}^{3}J_{3.4} = 7.7$ Hz, ${}^{4}J_{3.5} = 1.5$ Hz, 2 H, H_{py} -3), 7.86 (ddd, ${}^{3}J_{4'.3'} = 8.0$ Hz, ${}^{3}J_{4'.5'} = 7.6$ Hz, ${}^{4}J_{4'.6'} = 1.7$ Hz, 2 H, H_{py} -4'), 7.78 (dd, ${}^{3}J_{5.4} = 7.5$ Hz, ${}^{4}J_{5.3} = 1.4$ Hz, 2 H, H_{py} -5), 7.45 (ddd, ${}^{3}J_{6'.5'} = 5.0$ Hz, ${}^{4}J_{6'.4'} = 1.7$ Hz, ${}^{5}J_{6'.3'} = 0.9$ Hz, 2 H, H_{py} -6'), 7.20 (ddd, ${}^{3}J_{5'.4'} = 7.5$ Hz, ${}^{3}J_{5'.6'} = 5.0$ Hz, ${}^{4}J_{5'.3'} = 1.0$ Hz, 2 H, H_{py} -5'), 6.78 (dd, ${}^{3}J_{5.4} = 3.3$ Hz, ${}^{4}J_{5.3} = 1.1$ Hz, 2 H, H_{pyr} -5), 6.26 (dd, ${}^{3}J_{3.4} = 1.6$ Hz, ${}^{4}J_{3.5} = 1.1$ Hz, 2 H, H_{pyr} -3), 5.89 (dt, J = 5.8 Hz, ${}^{3}J_{4.3} = 2.9$ Hz, ${}^{3}J_{4.3} = 2.9$ Hz, 2 H, H_{pyr} -4) ppm.

¹³**C** NMR (101 MHz, CDCl_3): $\delta = 153.10$ (s, 2 C, C_{py} -6), 149.14 (s, 2 C, C_{py} -2'), 147.33 (s, 2 C, C_{py} -2), 146.53 (d, 2 C, C_{py} -6'), 140.23 (d, 2 C, C_{py} -4), 138.67 (d, 2 C, C_{py} -4'), 134.20 (s, 2 C, C_{py} -2), 130.55 (d, 2 C, C_{py} -3), 125.30 (d, 2 C, C_{py} -5'), 121.04 (d, 2 C, C_{py} -3'), 117.80 (d, 2 C, C_{py} -5), 114.18 (d, 2 C, C^{py} -3), 110.32 (d, 2 C, C_{py} -4), 108.59 (d, 2 C, C_{py} -5) ppm.

S1.2.6 Synthesis of [Fe(pypypyr)₂].



Variant A (two-step synthesis: deprotonation and complexation) A mixture of 443 mg 6-(pyrrole-2-yl)-2-(pyridine-2'-yl)pyridine (2.00 mmol, 2 eq.) and potassium *tert*-butoxide was suspended in 11 mL abs. MeCN at 0 °C in the dark. After 75 min, the solvent was removed from the yellow suspension and the yellow solid dried *in vacuo* to give 554 mg of the deprotonated ligand that was still contaminated with solvent but nonetheless used without further purification. The ligand was dissolved in 40 mL abs. MeCN and a solution of 337 mg iron(II) tetrafluoroborate hexahydrate (1.00 mmol, 1 eq.) in 7 mL abs. MeCN was added and rinsed with a further 8 mL, upon which the solution instantly changed colour from yellow-orange to dark green. After 2.5 h stirring, 160 mL deoxygenated

water were added and the dark green, almost black suspension stirred for 30 min. Afterwards, the suspension was filtrated, the solid residue washed twice with 40 mL deoxy. H_2O each and dried *in vacuo*. The solid was dissolved in abs. DCM, filtrated and rinsed, using a total of 70 mL solvent. The solution was dried over MgSO₄, stirred for 30 min, filtrated, rinsed twice with 10 mL abs. DCM each and the solvent removed *in vacuo*. Optionally (batch 3, see section S2), the solid was suspended in 60 mL abs. Et₂O, heated to reflux for 60 min, filtrated, resuspended in 50 mL abs. Et₂O, stirred at 45 °C for 30 min, filtrated, washed with 20 mL abs. Et₂O and dried *in vacuo*. After finely pestling the powder, it was dried twice for 7 h and 8 h, respectively, at 160 °C *in vacuo* at a pressure of $2 \cdot 10^{-2}$ mbar and the product thus obtained as a dark green powder in a yield of 357 mg (0.719 mmol, 72 %).

Anal. Calcd for C₂₈H₂₀FeN₆: C, 67.76 %; H, 4.06 %; N, 16.93 %. Found (batch 2): C, 66.39 %; H, 4.36 %; N, 16.15 %. Found (batch 3): C, 66.34 %; H, 4.17 %; N, 16.65 %.

¹H NMR (400 MHz, CDCl₃): $\delta = 8.41$ (dt, ${}^{3}J_{3'.4'} = 7.9$ Hz, ${}^{4}J_{3'.5'} = 1.0$ Hz, ${}^{5}J_{3'.6'} = 1.0$ Hz, 2 H, H_{py} -3'), 8.30 (dd, ${}^{3}J_{3.4} = 7.7$ Hz, ${}^{4}J_{3.5} = 0.7$ Hz, 2 H, H_{py} -3), 7.99 (t, ${}^{3}J_{4.3} = 7.9$ Hz, ${}^{3}J_{4.3} = 7.9$ Hz, 2 H, H_{py} -4), 7.73 (dd, ${}^{3}J_{5.4} = 8.0$ Hz, ${}^{4}J_{5.3} = 0.7$ Hz, 2 H, H_{py} -5), 7.63 (ddd, ${}^{3}J_{4'.5'} = 8.0$ Hz, ${}^{3}J_{4'.5'} = 7.5$ Hz, ${}^{4}J_{4'.6'} = 1.5$ Hz, 2 H, H_{py} -4'), 7.06 (ddd, ${}^{3}J_{6'.5'} = 5.7$ Hz, ${}^{4}J_{6'.4'} = 1.4$ Hz, ${}^{5}J_{6'.3'} = 0.8$ Hz, 2 H, H_{py} -6'), 6.91 (ddd, ${}^{3}J_{5'.4'} = 7.1$ Hz, ${}^{3}J_{5'.6'} = 5.6$ Hz, ${}^{4}J_{5'.3'} = 1.2$ Hz, 2 H, H_{py} -5'), 6.64 (dd, ${}^{3}J_{5.4} = 3.5$ Hz, ${}^{4}J_{5.3} = 1.1$ Hz, 2 H, H_{pyr} -5), 5.57 (dd, ${}^{3}J_{4.5} = 3.5$ Hz, ${}^{3}J_{4.3} = 1.7$ Hz, 2 H, H_{pyr} -4), 5.20 (dd, ${}^{3}J_{3.4} = 1.6$ Hz, ${}^{4}J_{3.5} = 1.2$ Hz, 2 H, H_{pyr} -3) ppm.

HR-ESI-MS (+): m/z = 496.10855 [M]⁺ (calc.: 496.10934; I = 100 %).

Variant B (basic precursor) The *in-situ* generated precursor is extremely sensitive to air. Thus, the whole apparatus (from the addition of $LiN(SiMe_3)_2$ to FeCl₂ until the isolation of the product) was connected from the beginning and never changed (not even in counter-flow, as this also led to degeneration of the precursor as evident by the colour change from green to brown).

Under N₂ atmosphere and at -94 °C (acetone + N_{2(l)}), 0.6 mL *n*-BuLi (2.5 M solution in *n*-hexane, 1.5 mmol, 3.0 eq.) were added to a solution of 258 mg of bis(trimethylsily)amine (1.60 mmol, 3.2 eq.) in 3 mL abs. Et₂O. After 20 min of stirring, the colourless suspension was slowly warmed to room temperature over 60 min, then added to a suspension of 95.0 mg of FeCl₂ (750 µmol, 1.5 eq.) in 4 mL abs. Et₂O at -10 °C, rinsed twice with 2 mL abs. Et₂O each and stirred for 22 h while slowly warming to room temperature. The solvent was removed *in vacuo* from the brown suspension to yield a dark green, viscous substance. Destillation at 120 °C and $2 \cdot 10^{-2}$ mbar through a short, angled glass tube (heated with a heat gun) gave a dark green liquid that solidified upon cooling. At 0 °C, this solid was then dissolved in 2 mL abs. Et₂O and a solution of freshly purified pypypyrH (221 mg, 1.00 mmol, 2 eq.) in 10 mL abs. Et₂O was added and rinsed with 3 mL. After 70 min, the dark green precipitate was filtrated, washed with abs. Et₂O and then abs. *n*-pentane (each twice with 10 mL each) and dried *in vacuo* for 3 h. In a Schlenk tube, the dark green, almost black solid was further dried (two times 7 h each) at 150 °C and $2 \cdot 10^{-2}$ mbar, resulting in a yield of 158 mg (318 µmol, 64 %).

Anal. Calcd for C₂₈H₂₀FeN₆: C, 67.76 %; H, 4.06 %; N, 16.93 %. Found: C, 67.65 %; H, 4.19 %; N, 16.87 %.

IR (ATR): $\tilde{v} = 3086$ (vw), 3061 (w), 3024 (vw), 1593 (s), 1551 (w), 1538 (w), 1516 (s), 1467 (vw), 1443 (s), 1433 (m), 1379 (s), 1329 (w), 1390 (m), 1300 (s), 1279 (s), 1248 (w), 1195 (w), 1164 (m), 1155 (m), 1140 (m), 1113 (w), 1074 (w), 1055 (w), 1029 (s), 1020 (s), 1006 (m), 966 (w), 942 (m), 895 (w), 874 (w), 835 (w), 799 (m), 771 (m), 757 (s), 737 (s), 714 (s), 688 (s), 661 (m), 638 (m), 619 (w), 606 (m), 555 (w) cm⁻¹.

FT-Raman (KBr): $\tilde{v} = 3078$ (vw), 1595 (s), 1551 (m), 1538 (s), 1519 (w), 1470 (s), 1436 (vw), 1382 (m), 1331 (s), 1306 (s), 1284 (m), 1274 (m), 1250 (vw), 1197 (w), 1156 (m), 1142 (w), 1113 (w), 1083 (w), 1046 (w), 1033 (s), 1007 (s), 948 (vw), 896 (w), 802 (vw), 691 (w), 661 (m), 640 (m), 558 (w), 503 (vw) cm⁻¹.

¹**H NMR** (400 MHz, CDCl_3): $\delta = 8.40$ (br. s, 2 H, H_{py} -3'), 8.30 (br. s, 2 H, H_{py} -3), 7.99 (br. s, 2 H, H_{py} -4), 7.74 (br. s, 2 H, H_{py} -5), 7.62 (br. s, 2 H, H_{py} -4'), 7.06 (br. s, 2 H, H_{py} -6'), 6.90 (br. s, 2 H, H_{py} -5'), 6.65 (br. s, 2 H, H_{pyT} -5), 5.58 (br. s, H, H_{pyT} -4), 5.21 (br. s, 2 H, H_{pyT} -3) ppm.

¹³**C NMR** (101 MHz, CDCl₃): $\delta = 160.78$ (s, 1 C, C_{py} -6), 159.60 (s, 1 C, C_{py} -2'), 158.30 (s, 1 C, C_{py} -2), 151.74 (d, 1 C, C_{py} -6'), 139.06 (s, 1 C, C_{pyr} -2), 134.36 (d, 1 C, C_{py} -4'), 133.38 (d, 1 C, C_{py} -4), 130.46 (d, 1 C, C_{pyr} -3), 124.49 (d, 1 C, C_{py} -5'), 121.52 (d, 1 C, C_{py} -3'), 113.70 (d, 1 C, C_{py} -3), 112.72 (d, 1 C, C^{py} -5), 109.86 (d, 1 C, C_{pyr} -4), 109.12 (d, 1 C, C_{pyr} -5) ppm.

S1.3 Analytical methods

S1.3.1 Mößbauer spectroscopy.

The Mößbauer spectra were measured on a self-constructed spectrometer⁵ in linear transmission geometry. Driving force was based on the Mößbauer Drive System MR260A and the Mößbauer Velocity Transducer MVT-1000 of the Wissenschaftliche Elektronik GmbH, Starnberg. The source consists of ⁵⁷Co in a rhodium matrix with starting activity of 25 mCi. All shifts are relative to α -iron. Fitsuite 1.0.4⁶ was used to fit the spectra.

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Spectra above room temperature were recorded on powder samples in transmission geometry, utilizing a ca. 2 mCi ⁵⁷Co radiation source mounted on a constant-acceleration Mößbauer driving unit (WissEl GmbH). Temperature control was achieved by means of a vacuum oven with a vacuum of about 10⁻² mbar. These data were evaluated in the *Pi* Program package by Ulrich von Hörsten. The experimental doublet structure was reproduced using an electric field gradient quadrupole distribution with linearly correlated chemical shifts.

S1.3.2 Thermal analyses.

The DTA/TG measurements were performed in Al_2O_3 crucibles under nitrogen atmosphere (airflow 6 L/h) using an STA-1000 instrument from Linseis (heat rate 4 K/min). The instrument was calibrated using standard reference materials, and all measurements were corrected for buoyancy.

The DSC experiments were performed using a DSC 1 star system with STARe Excellence software from Mettler-Toledo AG under a dynamic nitrogen atmosphere in Al pans.

S1.3.3 X-ray powder crystallography.

Single XRPD measurements at room temperature were performed with Cu-K α_1 radiation ($\lambda = 1.540598$ Å) or Mo-K α_1 radiation ($\lambda = 0.71073$ Å) using a Stoe Transmission Powder Diffraction System (STADI P) that is equipped with a MYTHEN 1K detector and a Johansson-type Ge(111) monochromator. For temperature-dependent (TD) XRPD measurements, a capillary furnace from STOE was used (ramp rate: 50 K). The rotating quartz glass capillaries containing the samples (diameter 0.5 mm) were heated from 303 K to the final temperature of 703 K. Diffractograms were measured directly upon reaching the target temperature (temperature increments between measurements: 50 K up to 453 K, 20 K up to 594 K and 10 K up to the final temperature).

S1.3.4 Vibrational spectroscopy.

Temperature-dependent FIR spectra were recorded on an IFS v66/S with a helium cryostat and CsI windows. The compound was dispersed in a CsI pressing.

For Resonance Raman spectroscopic measurements, a Raman system T64000 from Horiba was used with an Ar/Kr mixed-gas laser operating at 532 nm. The compounds were crimped in KBr.

S1.3.5 Magnetic measurements.

Magnetic susceptibilities were obtained from the neat powder sample using a Quantum-Design MPMS-5 SQUID magnetometer equipped with a 5 T magnet in the range from 400 K to 2 K. The data are corrected for the diamagnetic contributions and the sample holder. For the LIESST effect studies, the fibre-optic sample holder (FOSH, Quantum Design) with a 200 W Hg(Xe) arc lamp, a filter wheel (filter 545 nm, fwhm: 30 nm), a shutter and a multicore fibre (all LOT Oriel) were used. About 1 mg powdered sample was placed in the standard FOSH sample holder. The temperature was scanned with a rate of 1 K/min and the magnetic moment was measured in an applied field of 5000 Oe. The data were corrected for diamagnetism of the sample and the sample holder and the temperature offset due to irradiation.

S1.3.6 UV/Vis spectroscopy.

UV/Vis spectra were recorded with a Cary 5000 spectrometer in transmission geometry. For the temperature dependence, a Konti cryostat with liquid nitrogen or helium and a TIC-304 MA temperature controller from CryoVac were used. Heating curves were measured in sweeping mode: the measurements were started ca. 1 K below the given temperature and ended at ca. 1 K above the given temperature. For illumination experiments, a 3x Luxeon LXML-PM01-0100 ($\lambda = 525$ nm, 900 mW) LED from Philips Lumileds and a 3x Roithner VL440-Emitter ($\lambda = 444$ nm, 1000 mW) LED from Roithner Lasertechnik were used. The LED construction was done by Sahlmann Photochemical Solutions.

The quartz glass film was prepared by sublimation of the sample under UHV conditions $(5 \cdot 10^{-8} \text{ mbar})$ from a Knudsen cell heated to 220 °C onto a quartz glass disk kept at room temperature over 23 h. The deposition was controlled with a quartz crystal microbalance (twice as far from the Knudsen cell as the sample) that showed a total frequency change of 350 Hz. According to STM images of previously deposited films of other spin-crossover complexes, a frequency change of 1 Hz very roughly corresponds to 1 nm of film thickness. Thus, the visibly green film probably had a thickness of ca. (300±150) nm.

The polystyrene films were prepared under inert atmosphere according to a procedure reported in the literature.⁷ Polystyrene pellets (ca. 2 g) were dissolved in abs. DCM (ca. 1 mL). A minimal amount of the sample (<1 mg) was then also dissolved in ca. 1 mL of abs. DCM (the colour of the solution is approximately equal to the colour of the resulting film). Afterwards, 50 μ L of the complex solution were added to 150 μ L of the polystyrene solution, thoroughly mixed and poured into a rubber O-ring so that surface tension barely kept the solution inside. The solvent evaporated at room temperature over the course of 24 h.

The pellets of the complex dispersed in KBr were prepared by mixing a minimal amount of the sample (<1 mg) with ca. 10-15 mg of dry KBr and finely grinding the mixture to a homogeneous powder. The powder was then pressed into a pellet with a hydraulic press. The pellets were coated with a thin layer of polystyrene by submerging them in a solution (prepared as described above) and removal of the solvent under ambient conditions over 24 h.

S1.3.7 NEXAFS spectroscopy.

The NEXAFS spectra were measured at the VEKMAG end-station of the beamline PM2 at BESSY II (Berlin). The powdered sample was pressed into indium foil and then transferred directly to the measurement chamber through a garage valve into position for x-ray measurements at normal and at magic angle incidence (54.7°). During the experiments, the pressure in the chamber was ca. 10^{-10} mbar. The x-ray light utilised was linearly p-polarised with a ring current of 297.8 mA and a photon flux of approximately $1.6 \cdot 10^9$ s⁻¹mm⁻². Excitation was performed using a LED light with a wavelength of 520 nm, an operating voltage of 3.5 V and a flux density estimated as $4.2 \cdot 10^{14}$ s⁻¹mm⁻² at the sample position. For presentational purposes, all the raw data shown in this staudy were smoothened using a LOESS regression (comparison of raw and smoothened data, see Fig. S18). The regression was performed in Origin⁸, setting the data area to 0.1.

S1.3.8 DFT calculations.

Calculations of the single molecules in the gas phase were carried out with the ORCA software package.^{9,10} The structures of the complexes $[Fe(pypypyr)_2]$, $[Zn(pypypyr)_2]$ and $[Fe(terpy)_2]^{2+}$ were either preoptimised using molecular mechanics with the UFF¹¹ force field as implemented in Avogadro,¹² followed by geometry optimization with semiempirical methods (PM7¹³) implemented in MOPAC2016¹⁴ or the crystal structures were used as a starting point. Geometry optimizations and the calculation of thermodynamics and vibrational modes were performed with ORCA at the B3LYP^{15–17}/def2-SVP^{18,19} level with the D3BJ dispersion correction,^{20,21} the RIJCOSX approximation, fine numerical integration grids (grid4 and gridX4 in ORCA nomenclature) and the CG solver. The singlepoint energies, MO energies and TD-DFT excited states were calculated with ORCA at the B3LYP^{*}/def2-QZVP^{18,19} (*ScalHFX = 0.092024) level with the RIJCOSX approximation and fine numerical integration grids. After thermal correction as obtained from the geometry optimization, the energy gap ΔE_{HL}^0 was obtained as an approximation for ΔH_{HL}^0 .

Table S1 DFT-calculated thermodynamic data of $[Fe(pypypyr)_2]$, used for an estimation of the half time of the excited LIESST state according to the inverse energy gap law

S1.3.9 Single-crystal structures.

A suitable crystal was selected and mounted on an XtaLAB Synergy, Dualflex, HyPix diffractometer. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using least-squares minimisation. All non-hydrogen atoms were refined anisotropically. The C-H H atoms were positioned with idealised geometry and were refined isotropically with $U_{iso}(H) = 1.2 U_{eq}(C)$ using a riding model.

S2 Batch comparison

Over the course of this study, several batches of $[Fe(pypypyr)_2]$ were synthesised, trying to obtain a chemically pure sample. To this end, several different experimental techniques and approaches were used. The chemical analysis of six of these batches is discussed in this section.

For the first three batches, the ligand was first deprotonated, isolated and then further reacted with an Fe(II) precursor. In the first batch, we used $Fe(OAc)_2$, whereas $Fe(BF_4)_2 \cdot 6H_2O$ was used in the other two batches (see Variant A in section S1.2.6). The third batch only differs from the second batch by an additional step of purification detailed in the experimental section. The fourth batch was our first attempt to replicate the synthesis of the Zn(II) analogue by using the precursor $[Fe(Et)_2(bipy)_2]$. In batch 5, we used the observation that the protonated ligand can be coordinated to Fe(II) (precursor: $Fe(OTf)_2$) and then deprotonated with a milder base (MeOLi). Finally, the experimental details of batch 6, the first chemically pure substance, are detailed in Variant B in section S1.2.6.

Almost all experiments described in this study were measured on batch 2, with the exceptions of SQUID magnetometry (batch 3), the UV/Vis experiments on the dispersions in polystyrene and KBr (batch 3), the Mößbauer spectra (batch 5 at 80 K and 300 K; batch 6 at 297 K and above), the DSC measurement (batch 6) and the temperature-dependent XRPDs (batch 6). As the experiments are compared with each other, it is important to show that they are chemically identical. Despite vastly different synthetic procedures, batches 1, 4 and 6 show almost identical MIR and Raman spectra (see Fig. S1a,b). Importantly, batch 2 shows a different Raman spectrum at first glance. However, this spectrum was obtained in a different experiment with a different apparatus, a different irradiation wavelength (532 nm instead of 1064 nm), with the compound crimped into KBr instead of pure on ATR and after heating up from 10 K. Furthermore, except for a few bands (i.e., 232 cm⁻¹), the spectra only differ in intensities. This may be caused by a difference in texture caused by the different conditions. This is validated by the fact that the XRPDs and Mößbauer spectra of batches 2 and 6 are almost identical (except for a slight difference in crystallinity in the XRPDs; see Fig. S1c,d). However, batch 3 shows two additional reflexes below $5^{\circ}2\theta$. Such a notable impurity may influence the SQUID magnetometric data measured on this batch. However, looking at the NMR spectra (see Fig. S1e), this impurity is most probably not a different iron species, since the spectrum shows no sign of paramagnetism. Instead, it appears to contain traces of at least MeCN and KBF (19 F spectrum, not shown). While the elemental analysis may be explained by



Fig. S1 Comparison of the chemical analytics of different batches of $[Fe(pypypr)_2]$ with MIR spectroscopy (a), Raman spectroscopy (b), XRPDs (c), Mößbauer spectroscopy (d) and NMR spectroscopy (e). In all cases, the spectra are offset vertically and sometimes scaled differently to increase comparability. The Raman spectrum of batch 2 was measured with 532 nm irradiation instead of the 1064 nm used for the other batches. The XRPDs were all recorded with Mo-K α_1 radiation. All NMR spectra were measured in DMSO-d₆ and referenced to the residual protonated solvent signal. Traces of solvents are labelled.

additional traces of DCM and water, they are both difficult to prove with the NMR spectrum. DMSO-d₆ always contains water and other deuterated solvents at hand did not provide sufficient solubility. Additionally, we found that even freshly bought and unsealed DMSO-d₆ contained traces of DCM. Comparing the NMR spectra of all the batches, an interesting yet not fully understood phenomenon is observed. In some batches, the proton signals are broadened as if a slightly paramagnetic substance was present. However, not all signals are equally affected: five of the signals are broader than others and shifted upfield in batches 2 and 5 (and others not shown), whereas they do not shift in batches 1 and 6 despite them being broadened the most of the batches. Also, batch 6 is broadened the most despite being chemically pure. We attribute this broadening to the sensitivity of the compound in solution and oxidation by air (although sealed tubes and degassed solvents were used).

Overall, chemical analysis indicates that, aside from trace impurities, the samples of $[Fe(pypypyr)_2]$ are always comparable and do not contain a variable mixture of different phases despite vastly different experimental protocols. Unexplained differences were observed in solution by NMR spectroscopy. However, only the polystyrene film used in UV/Vis spectroscopy was dissolved during the preparation of the sample. Furthermore, batches 2 and 3 were dissolved in DCM during the synthesis, whereas batch 6 was never dissolved in any solvent. Still, they appear to be the same by chemical analysis. As such, solvation and subsequent removal of the solvent do not appear to influence the state of the complex. Aside from this behaviour in solution, the only other indication of different behaviour is found for the Raman spectrum of batch 2. However, this is unlikely to be caused by pressure applied on the KBr pellet. Batches 2 and 3 were strongly pestled between the drying phases, whereas batch 6 was not treated mechanically at all. Still, they show identical XRPDs. As such, the data discussed in this study is unlikely to be heavily influenced by polymorphism. This is in agreement with the fact that the high variety of methods and treatments of the sample yield rather consistent results.

S3 Analytical data

S3.1 Miscellaneous data



Fig. S2 Mößbauer spectra of $[Fe(pypypyr)_2]$ at a) 80 K and b) 300 K. The respective isomer shift δ and quadrupole splitting ΔE_Q are given. With a different setup (300 K spectrum for reference in panel c), we were able to heat up to 510 K (d). No major change occurs in the spectral shape upon heating which warrants the conclusion that no SCO occurs until 510 K for $[Fe(pypypyr)_2]$.



Fig. S3 Thermoanalytical data of $[Fe(pypypyr)_2]$. a) Combination of simultaneously measured differential thermal analysis (DTA, red) and thermogravimetry (TG, black). The first derivative of the TG is also given (DTG, grey) to increase the visibility of small changes. This analysis was performed on an early sample that still included some residual solvent (DCM) as apparent from NMR spectroscopy. Accordingly, the first two events with a loss of sample mass before 440 K can be attributed to the removal of said solvent. Starting at 450 K, a gradual loss of sample mass occurs that has no clearly distinct steps and never ends until 880 K. This gradual loss of sample mass can be attributed to sublimation of the sample. At ca. 630 K, a distinct endothermic event occurs that does not coincide with a mass loss. b) Differential scanning calorimetry heating and cooling curves between 298 K and 723 K. Similar to the DTA results, only one endothermic event is observed at ca. 635 K. However, this event is not reversible upon cooling. Thus, this event cannot be attributed to a spin-crossover and is most likely caused by thermal decomposition of the sample.



Fig. S4 X-ray powder diffractograms (XRPDs) of [Fe(pypypyr)₂] (Cu-K α_1 radiation; diffractograms shifted vertically for clarity). a) The pristine powder as synthesised (blue) shows low crystallinity, but a distinctly different reflex pattern than the diffractogram calculated from the single-crystal structure (black), proving that the powder does not share the same structure. After heating the powder to 618 K (slightly before thermal decomposition), a diffractogram back at 300 K (green) shows drastically increased crystallinity. This can be explained by restructuring at high temperatures, potentially via sublimation and resublimation. At 634 K, however, the diffractogram looks very similar but not identical to the reflex pattern at 300 K: all reflexes are shifted to slightly lower 2 θ values, there are three instead of two reflexes at ca. 12° and while, at 300 K, the reflex with lower intensity at around 11° is on the right side of the reflex with the higher intensity, it is on the left side at 634 K. b) Evolution of the XRPDs upon heating from 303 K to 663 K. Up until ca. 603 K, the only change in the diffractograms is a shift to slightly lower 2 θ values. After this temperature, the crystallinity slowly starts to increase, leading to the XRPD that is slightly different from the XRPD at 300 K (as described above). Between 634 K and 643 K, the overall intensity of the XRPDs starts to increase until the sample becomes x-ray amorphous at 663 K, further evidencing a thermal decomposition of the sample.



Fig. S5 FIR (550-150 cm⁻¹) spectra of $[Fe(pypypyr)_2]$ at 300 K (red), 100 K (blue) and 10 K (green). The spectra are identical at all temperatures within the accuracy of the experiment (spectra shifted vertically for clarity).

We also investigated the thermal spin-crossover and LIESST behaviour of $[Fe(pypypyr)_2]$ in the bulk material using vibrational spectroscopy. The bond lengths between the metal centre and the coordinating ligand atoms typically increase by about 0.2 Å upon spin transition from low-spin to high-spin due to higher occupation of the anti-bonding e_g orbitals. This bond elongation results in a drastic change of energy for the vibrational modes that include these bonds. Hence, the vibrational spectrum of an LS compound is expected to look different compared to the HS spectrum, i.e., some vibrational modes differ in intensity and energy, especially in the low-energy region below 1000 cm⁻¹, where metal-ligand vibrations are more dominant.

First, we measured FIR spectra at 300 K, 100 K and 10 K. According to the results from all other methods, no thermal spin transition between 10 K and 300 K was expected, so the spectra should be identical. Indeed, there are only minor differences that cannot be attributed to a spin change (see Fig. S5). However, temperature-dependent resonance-Raman spectroscopy led to different results. Using a laser with a wavelength of 532 nm for the Raman excitation, occurrence of the LIESST effect is expected at low temperatures. Fig. S6 shows the measured spectra at 300 K, 100 K and 10 K. The former two are identical within the error margin of the experiment, while the latter varies noticeably. To evaluate these results further, aside from the visual perspective, we compared the measured vibrational modes to the vibrational modes from DFT calculations for both states. Direct assignment of vibrational modes is typically vague at best, but fortunately not necessary to evidence a spin transition. Instead, we compared the calculated spectra for both spin states by calculating the difference between the vibrational energy for every vibrational mode in both states, i.e., subtracting the calculated vibrational energy for a given mode in the LS state from the calculated energy in the HS state. These values then allowed us to determine where in the spectrum noticeable changes are expected. As expected from the theory described above, the differences are rather small in the high-energy region above 700 cm⁻¹. The highest difference is -20.9 cm⁻¹ and the majority of vibrational modes differ by less than 14 cm⁻¹ in either direction (see Table S3). The vibrational modes with the highest differences between the spin states are shown in Fig. S6 as green or red bars, with the colour indicating their value. Since the vibrational energies from DFT calculations are typically rather accurate relative to each other but the absolute values may differ from the experiment, the calculated energies were shifted by -60 cm^{-1} for the comparison. That way, the calculated results fit the observed differences in the spectra very well.

The same analysis was done for the low-energy region, where the differences between the two spin states are, in agreement with the above-described expectations, much higher: the majority of the differences is between 10 cm^{-1} and 140 cm^{-1} , while the highest difference is -176.5 cm⁻¹ (see Table S2). Additionally, this region is, opposed to the high-energy region, dominated by shifts to lower energies from the LS to the HS state. This can be explained by the higher occupation of anti-bonding e_g orbitals in the HS state, which leads to lower bond orders and bond strengths of the Fe-N bonds that have a more prominent role in this region, resulting in lower vibrational energies. Accordingly, the vibrational modes with the highest differences in the calculations are either asymmetric *trans*-N-Fe-N stretching modes (see Fig. S7) or vibrational modes where the whole complex deforms heavily (see Fig. S8). For the comparison with the calculated data, we identified four major potential shifts in the experimental data. The two bands at 378 cm⁻¹ and 342 cm⁻¹ in the 300 K and 100 K spectra vanish in the 10 K spectrum, whereas two new bands appear in the 10 K spectrum at 243 cm⁻¹ and 203 cm⁻¹. The location and the difference between these two sets of bands (-135 cm⁻¹ and -139 cm⁻¹, respectively), both, fit very well



Fig. S6 Resonance Raman spectra of $[Fe(pypypyr)_2]$ at 300 K (red), 100 K (blue) and 10 K (green) with an excitation wavelength of 532 nm in the high-energy region (1690-750 cm⁻¹, left) and the low-energy region (750-90 cm⁻¹, right). Coloured bars highlight bands that only appear in or have significantly higher intensities in the 300 K and 100 K spectra (blue, assigned to the LS state) or in the 10 K spectrum (red, assigned to the HS state). Higher transparency of these bars indicates a lesser difference in intensities between the spectra. The red and green lines in the dark grey portions above the spectra represent DFT-calculated vibrational modes. Their position indicates the wavenumber of the vibrational mode as derived from the calculations of the LS state with a shift of -60 cm⁻¹. The colour indicates the difference between the calculated wavenumber in the HS state and the LS state, according to the scales on the outer sides of the respective spectra.

with the calculations. However, the absence of the band at 655 cm⁻¹ and the emergence of the two bands at 577 cm⁻¹ and 532 cm⁻¹ are not in accordance with the calculations. The differences in the spectra between 400-500 cm⁻¹ have been neglected, since in this region the data at 300 K and 100 K also differ significantly. Therefore, it is unclear which part of these changes is due to the spin transition.

In summary, the experimental data show significant changes in the intensity and location for several bands that are in good agreement with DFT calculations and can thus be assigned to a light-induced spin transition. Although this data, just like the above measurements, cannot be used to quantify the bulk HS fraction in absolute values, the near-complete disappearance of the bands at 342 cm⁻¹, 379 cm⁻¹, 656 cm⁻¹ and 1015 cm⁻¹ in the 10 K spectrum (see Fig. S6, all highlighted with blue bars) indicates that the HS fraction during irradiation with 532 nm is close to 100 %.



Fig. S7 Vibrational mode of $[Fe(pypypyr)_2]$ with an energy of 390.24 cm⁻¹ in the LS state in its two end states with maximum deflection. The involvement of each atom is indicated by a scaled vector (blue arrows). Elements: Fe, orange; N, blue; C, grey; H, white. The main component of this vibrational mode is the asymmetric stretching mode of *trans*-N_{pyr}-Fe-Npy.



Fig. S8 Vibrational mode of $[Fe(pyppyr)_2]$ with an energy of 366.45 cm⁻¹ in the LS state in its two end states with maximum deflection. The involvement of each atom is indicated by a scaled vector (blue arrows). Elements: Fe, orange; N, blue; C, grey; H, white. This vibrational mode involves strong distortion of the ligands and metal-ligand bonds, both.

Table S2 DFT-calculated vibrational modes of the LS and HS state, respectively, of $[Fe(pyppyr)_2]$ in the energy range below 750 cm⁻¹. The vibrational modes are sorted by the energy in the LS state in descending order. The vibrational energies in the HS state have been assigned accordingly by comparing the visualised vibrational modes using ChemCraft. The difference between those values $(\Delta \tilde{v}_{HS-LS})$ is colour-coded using a gradient from -140 cm⁻¹ (red) to +140 cm⁻¹ (green)

\tilde{v}_{calcLS} / cm ⁻¹	$\tilde{v}_{\text{calc.,HS}}$ / cm ⁻¹	$\Delta \tilde{v}_{\text{HS-LS}}$ / cm ⁻¹	$\tilde{v}_{\text{calc.,LS}}$ / cm ⁻¹	\tilde{v}_{calcHS} / cm ⁻¹	$\Delta \tilde{v}_{\text{HS-LS}}$ / cm ⁻¹
738.75	739.12	0.37	367.17	229.69	-137.48
738.18	738.88	0.70	366.45	125.45	-241.00
709.40	713.43	4.03	347.50	325.77	-21.73
706.63	701.31	-5.32	328.40	373.32	44.92
706.24	700.57	-5.67	319.65	277.36	-42.29
703.85	712.65	8.80	316.81	279.16	-37.65
681.03	669.21	-11.82	269.15	231.97	-37.18
678.51	669.24	-9.27	260.27	243.44	-16.83
654.98	637.58	-17.40	259.75	371.96	112.21
651.63	639.40	-12.23	238.26	225.16	-13.10
643.12	645.16	2.04	227.70	266.63	38.93
634.68	641.30	6.62	204.71	145.75	-58.96
619.12	620.63	1.51	200.12	151.97	-48.15
618.51	620.09	1.58	184.87	153.62	-31.25
566.62	547.88	-18.74	162.29	115.72	-46.57
565.65	547.47	-18.18	149.04	95.54	-53.50
516.75	505.20	-11.55	133.92	107.36	-26.56
515.09	504.88	-10.21	124.28	106.35	-17.93
503.96	455.91	-48.05	113.57	121.83	8.26
495.47	451.44	-44.03	93.35	79.77	-13.58
482.93	453.75	-29.18	91.93	67.93	-24.00
479.62	448.34	-31.28	52.77	44.40	-8.37
456.75	340.94	-115.81	50.88	42.09	-8.79
452.85	426.57	-26.28	34.95	24.21	-10.74
447.36	423.68	-23.68	33.09	24.61	-8.48
397.56	247.03	-150.53	30.18	16.41	-13.77
390.24	213.77	-176.47			

Table S3 DFT-calculated vibrational modes of the LS and HS state, respectively, of $[Fe(pypypyr)_2]$ in the energy range above 750 cm⁻¹. The vibrational modes are sorted by the energy in the LS state in descending order. The vibrational energies in the HS state have been assigned accordingly by comparing the visualised vibrational modes using ChemCraft. The difference between those values ($\Delta \tilde{v}_{HS-LS}$) is colour-coded using a gradient from -14 cm⁻¹ (red) to +14 cm⁻¹ (green)

$\tilde{v}_{calc.,LS}$ / cm ⁻¹	$\tilde{v}_{\text{calc.,HS}}$ / cm ⁻¹	$\Delta \tilde{v}_{\text{HS-LS}}$ / cm ⁻¹	\tilde{v}_{calcLS} / cm ⁻¹	\tilde{v}_{calcHS} / cm ⁻¹	$\Delta \tilde{v}_{\text{HS-LS}}$ / cm ⁻¹
3235.06	3233.85	-1.21	1302.74	1304.84	2.10
3234.88	3233.54	-1.34	1221.61	1220.02	-1.59
3219.03	3217.03	-2.00	1221.26	1217.45	-3.81
3218.74	3216.72	-2.02	1189.22	1185.53	-3.69
3216.77	3222.32	5.55	1188.40	1183.22	-5.18
3216.40	3222.39	5.99	1166.98	1171.71	4.73
3214.46	3210.69	-3.77	1166.77	1171.47	4.70
3214.10	3210.85	-3.25	1162.42	1164.70	2.28
3209.81	3213.37	3.56	1162.27	1165.00	2.73
3209.56	3213.51	3.95	1140.45	1141.41	0.96
3207.67	3204.92	-2.75	1138.69	1139.19	0.50
3207.54	3204.72	-2.82	1105.71	1109.46	3.75
3206.67	3208.44	1.77	1105.08	1109.14	4.06
3206.64	3208.57	1.93	1092.67	1100.70	8.03
3202.28	3198.42	-3.86	1090.82	1100.09	9.27
3201.84	3198.32	-3.52	1075.28	1077.64	2.36
3189.65	3186.57	-3.08	1074.06	1076.54	2.48
3189.55	3186.72	-2.83	1062.90	1066.64	3.74
3181.52	3181.09	-0.43	1062.51	1063.55	1.04
3181.43	3180.83	-0.60	1049.32	1028.42	-20.90
1659.15	1656.65	-2.50	1048.74	1050.34	1.60
1657.26	1655 35	-1.91	1048 52	1049 95	1 43
1653 53	1650 10	-3.43	1039.90	1021 43	-18 47
1652 56	1650.34	-2.22	1035 11	1019 32	-15 79
1617.63	1626.88	9.25	1030.23	1017.32	-5.93
1616.88	1627.35	10.47	1010 21	1024.0	7 20
1500.82	1602 94	3 12	1019.21	1026.41	6.84
1508 75	1602.54	3.87	1017.17	1020.01	0.04
1577.85	1578 77	0.92	1000.02	1010.34	9.72
1577.68	1577 25	-0.43	983 29	990 23	6.94
1516.13	1510.44	-5.69	983.07	990.07	7.00
1512 42	1509.88	-2 54	968 50	965 33	-3.17
1508 54	1502.14	-6.40	966.05	964 74	-1 31
1504 59	1497 78	-6.81	916 72	914 52	-2.20
1483 15	1483.92	0.77	916 58	914 77	-1.81
1482.40	1483.22	0.73	904.65	008.80	4 94
1478 36	1474 32	-4.04	904 56	008.07	4 41
1477 23	1474 63	-2.60	887.02	807.22	0.30
1432.06	1434 25	1 20	887.46	807 14	9.68
1429 62	1430.97	1.25	886.21	893.86	7.65
1422.02	1421 40	-0.69	885 58	893 73	8 15
1420.65	1421.10	0.79	831.01	843 44	12.43
1383.60	1387 20	3.60	830.03	842 54	11.61
1382 52	1385 20	2 77	825 73	874 73	-1.00
1360.05	1366.86	5.01	825 11	824.50	-1.00
1360.60	1361.05	1.26	821.25	832.28	11.03
1353 53	1338 50	-15.03	820.27	832.20	11.05
1252.02	1220 15	12.03	782 58	702.04	10.68
1332.70	1337.13	5.87	781 34	702 57	11.00
1222.72	1327./7	5.07	772 50	760 53	4.06
1323.//	1210.28	0.09	768 58	767 55	1.03
1320.25	1317.50	-2.01	750.37	756.05	5.68
1317.03	1206.00	0.55	750.57	755.26	5.00
1000.00	1000.00	-0.55	/ 50.15	/ 55.50	5.21



Fig. S9 SQUID magnetometric data of $[Fe(pypypyr)_2]$. a) Excitation via irradiation with 545 nm. The data are fitted using mono- (black), bi- (red) and triexponential (green) growth fits. The resulting adjusted R² values are given as a measure of the fit quality. b) Relaxation at 5 K in darkness. The data are fitted using mono- (black), bi- (red) and triexponential (green) decay fits. The resulting adjusted R² values are given as a measure of the fit quality. b) Relaxation at 5 K in darkness. The data are fitted using mono- (black), bi- (red) and triexponential (green) decay fits. The resulting adjusted R² values are given as a measure of the fit quality. All three relaxation fits (marked with *) were obtained by including an imaginary data point at 10000 min ($\gamma_{HS} = 0$) to force asymptotic behaviour approaching zero.

The LIESST excitation data were fitted using mono-, bi- and triexponential growth functions (see Eq. S1). Monoexponential behaviour poorly describes the data, especially in the first 7 min. Biexponential behaviour describes the data better, but still shows some discrepancies, with the initial increase being too steep and the function being too flat later on. These flaws do not occur in triexponential behaviour that represents the data very well.

$$\gamma_{\text{HS,exc.}} = \gamma_{\text{HS,\infty}} - (A_1 \cdot e^{-t/t_1} + A_2 \cdot e^{-t/t_2} + A_3 \cdot e^{-t/t_3})$$
(S1)

$$\gamma_{\rm HS\ mono} = 0.903 - (0.512 \cdot e^{t/(8.101\ \rm{min})}) \tag{S2}$$

$$\gamma_{\rm HS \ bi} = 0.947 - (0.451 \cdot e^{t/(0.272 \ {\rm min})} + 0.469 \cdot e^{t/(12.159 \ {\rm min})}) \tag{S3}$$

$$\gamma_{\rm HS tri} = 1.000 - (0.330 \cdot e^{t/(0.090 \text{ min})} + 0.213 \cdot e^{t/(1.348 \text{ min})} + 0.457 \cdot e^{t/(17.681 \text{ min})})$$
(S4)

The isothermal relaxation data were also fitted using mono-, bi and triexponential decay functions (see Eq. S5). Once again, monoexponential behaviour does not represent the data very well. The difference between bi- and triexponential behaviour is neglectable in this case.

$$\gamma_{\rm HS, relay} = A_1 \cdot e^{-t/t_1} + A_2 \cdot e^{-t/t_2} + A_3 \cdot e^{-t/t_3} \tag{S5}$$

$$\gamma_{\rm HS,mono} = 0.959 \cdot e^{-t/(266.351 \text{ min})}$$
 (S6)

$$\gamma_{\rm HS,bi} = 0.061 \cdot e^{-t/(3.722 \text{ min})} + 0.932 \cdot e^{-t/(406.853 \text{ min})}$$
(S7)

$$\gamma_{\rm HS,tri} = 0.023 \cdot e^{-t/(0.699 \, \text{min})} + 0.056 \cdot e^{-t/(5.798 \, \text{min})} + 0.924 \cdot e^{-t/(469.115 \, \text{min})}$$
(S8)

S3.4 Additional UV/Vis spectra and data evaluation

Table S4 Bond lengths between the central Fe(II) ion and the coordinating N atoms in $[Fe(terpy)_2](CIO_4)_2 \cdot H_2O$ at 283-303 K,²² 243 K²³ and 100 K²⁴. The change in bond lengths has also been extrapolated to the temperature of 5 K ($\Delta_{r,300-5}$). Furthermore, this change is given in relation to a typical expansion of 0.2 Å during spin transition in spin-crossover compounds (Δ_T)

	<i>r</i> _{Fe-N} (283-303 К) / Å	<i>r</i> _{Fe-N} (243 К) / Å	<i>r</i> _{Fe-N} (100 К) ∕ Å	$\Delta_{r,300-5}$ / Å	Δ_T / %
control puriding	1.891	1.887	1.882	0.013	6.4
central pyridine	1.890	1.888	1.885	0.007	3.6
	1.988	1.988	1.984	0.006	3.2
toursin of newidin o	2.001	1.990	1.983	0.024	12.1
terminal pyridine	1.984	1.981	1.974	0.015	7.4
	1.978	1.990	1.979	0.004	1.9



Fig. S10 Bond lengths between the central Fe(II) ion and the coordinating N atoms (black: central pyridine; red and blue: terminal pyridines) in $[Fe(terpy)_2](CIO_4)_2 \cdot H_2O$ at 283-303 K,²² 243 K²³ and 100 K.²⁴ Dark colours represent one ligand and light colours the other.

Similar to the results from SQUID magnetometry, the isothermal relaxation data from UV/Vis spectroscopy were fitted using mono-, bi and triexponential decay functions (see Eq. S9). Yet again, the triexponential fit describes the data the best, although an imaginary data point was necessary to force asymptotic behaviour.

$$\gamma_{\rm HS \ relax} = A_1 \cdot e^{-t/t_1} + A_2 \cdot e^{-t/t_2} + A_3 \cdot e^{-t/t_3}$$
(S9)

$$\gamma_{\rm HS\,mono} = 0.762 \cdot e^{-t/(220.900\,\,{\rm min})}$$
(S10)

$$\chi_{\rm IS \ bi} = 0.276 \cdot e^{-t/(7.611 \ \rm{min})} + 0.672 \cdot e^{-t/(294.674 \ \rm{min})}$$
(S11)

$$\gamma_{\rm HS,tri} = 0.220 \cdot e^{-t/(2.240 \text{ min})} + 0.351 \cdot e^{-t/(58.951 \text{ min})} + 0.431 \cdot e^{-t/(1272.083 \text{ min})}$$
(S12)



Fig. S11 a) UV/Vis spectra of $[Fe(pypypr)_2]$ for three different preparation methods: a thick film deposited on quartz glass via PVD, a dispersion in polystyrene and a dispersion in KBr. All samples were irradiated at 5 K using a wavelength of 440 nm for 1 min and then heated up to 100 K in darkness. b) Extracted HS fractions relative to the lowest observed absorbance of the band at ca. 684 nm for the three experiments shown in panel a. The experiment on quartz glass was repeated with an optimised method that allowed the first measurement to be taken ca. 5 s instead of 1 min after switching off the LED (black stars). In all four cases, there is a reproducible discontinuity, where the intensity first decreases and then increases rapidly, before going back to the expected behaviour. This discontinuity happens in a range of ca. 20 K, roughly centred on T_{LIESST} . The extracted HS fractions below 0.0 (down to -0.7) and above 1.0 (up to 5.3) are indicated in the bars below and above the normal range and are not up to scale. The dotted lines are guidelines to the eye that show the general course of the HS fractions during the discontinuity, which is identical in all four cases, albeit a lot less pronounced in the PS film.



Fig. S12 a) UV/Vis spectra of $[Fe(pypypyr)_2]$ on quartz glass at 295 K (black), 5 K (blue) and after irradiation with 530 nm (red). At all temperatures, multiple spectra were taken with varying intensity levels of the measuring beam between 10 % and 1000 % of the standard intensity used for all other spectra. The spectra were standardised to the isosbestic point at 555 nm. b) UV/Vis spectra of the thermal relaxation with the intensity of the measuring beam at 30 % of the standard value.



Fig. S13 a) UV/Vis spectra of [Fe(pypypr)₂] on quartz glass during the isothermal relaxation at 5 K after irradiation with 530 nm. The spectrum after 1 min, as well as some spectra not shown, show an irregularity in the absorbance below 590 nm. This was caused by an unknown problem with the spectrometer during this set of measurements. Only spectra without irregularities between 750 nm and 630 nm were used for the determination of the relaxation rate. Aside from this problem, there is also a noticeable gap between the spectra at 30 min and at 62 min in the band at 417 nm. b) Plot of the HS fractions as determined from the spectra partially shown in panel a. The data were fitted using mono- (black), bi- (red) and triexponential (green) fits. The triexponential fit (marked with *) was obtained by including an imaginary data point at 5000 min ($\gamma_{HS} = 0$) to force asymptotic behaviour approaching zero. The adjusted R² values are given. The inlay in the top right shows a wider x range.



Fig. S14 a) Plot of the elapsed time against the temperature for the thermal relaxation measurement to determine the heat rate. b) Relative HS fractions during the thermal relaxation measurement (green dots). The data used for the determination of the function describing the spin state-independent increase in absorbance (black line and dots, see Eq. 7) are highlighted in black. The data were fitted using Eq. 3 (green line). The first derivative of the fit is given in red. This figure shows the same data as the inlay in Fig. 4c as a full panel.

S3.5 TD-DFT calculations

To further evidence the identity of the bands in the UV/Vis spectra of $[Fe(pypypr)_2]$, we employed TD-DFT calculations. Thereby, we were able to determine excited states and the respective involved molecular orbitals. The resulting simulated spectra of the two spin states (see Fig. S15) show vague agreement with the experimental spectra, with the highest intensities below 400 nm and the bands above 400 nm more spread out and less intense. The agreement between the calculated and experimental spectra is better for the LS state. Calculation of the excited states of the HS states seems to underestimate (higher wavelengths) the energy of the bands in the low-energy region. More detailed analysis of the excited states and assignment of transition types (see Table S5 and Table S6), however, results in a good agreement with the expectations: the excitations with the highest relative weights show minimal involvement of d-d transitions. Instead, the low-energy region above 400 nm is almost exclusively dominated by charge-transfer transitions, whereas the high-energy region below 400 nm is dominated by ligand-centred transitions. The same qualitative result is also obtained from the comparison of the complex spectra with the spectrum of the pure ligand (see ESI†, Fig. 4a), which does not show any bands above 400 nm.



Fig. S15 a) Comparison of the experimental UV/Vis spectrum at 5 K in darkness (blue) with a theoretical absorption spectrum of the LS state of $[Fe(pypypyr)_2]$ determined with TD-DFT. Individual transitions are given as black bars with their respective intensity. Gaussian broadening with a band width of 15 nm at 50 % of the max intensity of each transition was applied to simulate the spectrum (black line). b) Comparison of the experimental UV/Vis spectrum at 5 K after 2 min of irradiation with 532 nm (red) with a theoretical absorption spectrum of the HS state of $[Fe(pypypr)_2]$ determined with TD-DFT. Individual transitions are given as black bars with their respective intensity. Gaussian broadening with a band width of 20 nm at 50 % of the max intensity of each transition was applied to simulate the spectrum (black line).



Fig. S16 Exemplary calculated MOs. MOs were loosely sorted into four categories: MOs with electron density almost exclusively on ligands (a) or metals (d) and hybrid orbitals with electron density mostly on ligands (b) or metals (c). One example from each category is shown.

Table S5 Excited states of the LS state of $[Fe(pypypyr)_2]$ as determined with TD-DFT. For each state, the wavelength λ , the intensity, the two excitations with the highest weight and the assigned type of transition are given. For each excitation, the two involved molecular orbitals and their respective assignments are given, as well as their weight.

			excitation 1			excitation 2		
λ/nm	intensity / a. u.	MO numbers	MO types	weight / %	MO numbers	MO types	weight / %	assignment
704.0	11.26	$128 \rightarrow 129$	$d_{xy} \rightarrow L + d_{yz}$	72.4	126→129	$d_{xz} \rightarrow L + d_{yz}$	18.0	MLCT
683.0	2.68	$128 { ightarrow} 130$	$d_{xy} \rightarrow L + d$	47.5	$126 \rightarrow 130$	$d_{xz} ightarrow L + \dot{d}$	36.1	MLCT
642.1	0.42	$126 { ightarrow} 130$	$d_{xz} \rightarrow L + d$	38.0	$127 \rightarrow 129$	$d_{vz} \rightarrow L + d_{vz}$	28.5	MLCT
637.3	5.63	$127 \rightarrow 130$	$d_{vz} \rightarrow L + d$	42.2	$126 \rightarrow 129$	$d_{xz} \rightarrow L + d_{vz}$	36.2	MLCT
610.8	37.8	$126 \rightarrow 129$	$d_{xz} \rightarrow L + d_{vz}$	37.4	$127 \rightarrow 130$	$d_{vz} \rightarrow L + \dot{d}$	27.8	MLCT
580.8	1.52	$127 \rightarrow 129$	$d_{vz} \rightarrow L + d_{vz}$	53.5	$128 \rightarrow 130$	$d_{xv} \rightarrow L + d$	28.8	MLCT
534.1	0.46	$125 \rightarrow 130$	$d_{vz} + L \rightarrow L + d$	21.7	$126 \rightarrow 138$	$d_{xz} \rightarrow d_{z^2} + L$	15.4	MLCT + d-d
526.3	0.62	$125 \rightarrow 129$	$d_{vz} + L \rightarrow L + d_{vz}$	53.1	$124 \rightarrow 130$	$d_{xz} + L \xrightarrow{z} L + d$	23.7	MLCT
522.6	2.73	$125 \rightarrow 130$	\dot{d}_{vz} + L \rightarrow L + \dot{d}	38.5	$126 \rightarrow 138$	$d_{xz} \rightarrow d_{z^2} + L$	11.6	MLCT + d-d
505.2	9.23	$124 \rightarrow 129$	$d_{xz} + L \rightarrow L + d_{vz}$	43.1	$128 \rightarrow 131$	$d_{xv} \xrightarrow{L} L$	36.4	MLCT
495.5	16.11	$128 \rightarrow 131$	$d_{xv} \rightarrow L$	46.0	$124 \rightarrow 129$	$d_{xz} + L \rightarrow L + d_{vz}$	27.7	MLCT
486.3	0.55	$128 { ightarrow} 132$	$d_{xv} \rightarrow L$	33.1	$124 \rightarrow 130$	$d_{xz} + L \rightarrow L + \dot{d}$	28.8	MLCT
473.4	10.94	$127 \rightarrow 131$	$d_{vz} \rightarrow L$	64.7	$128 \rightarrow 132$	$d_{xv} \rightarrow L$	9.2	MLCT
465.5	11.25	$126 \rightarrow 131$	$d_{xz} \rightarrow L$	72.1	$127 \rightarrow 132$	$d_{vz} \rightarrow L$	10.2	MLCT
463.2	0.3	$124 \rightarrow 139$	$d_{xz} + L \rightarrow d_{z^2}$	24.1	$125 \rightarrow 138$	$d_{vz} + L \rightarrow d_{z^2} + L$	11.8	MLCT + d-d
460.2	0.67	$125 \rightarrow 139$	$d_{vz} + L \rightarrow d_{z^2}$	24.7	$124 \rightarrow 138$	$d_{xz} + L \rightarrow d_{z^2} + L$	14.1	MLCT + d-d
455.5	2.98	$128 \rightarrow 132$	$d_{xv} \rightarrow L^{2}$	45.5	$127 \rightarrow 131$	$d_{vz} \rightarrow L^{z}$	13.7	MLCT
443.7	11.82	$127 \rightarrow 132$	$d_{vz} \rightarrow L$	71.2	$125 \rightarrow 132$	$d_{vz} + L \rightarrow L$	5.8	MLCT
439.4	4.65	$126 \rightarrow 132$	$d_{xz} \rightarrow L$	71.9	$128 \rightarrow 133$	$d_{xy} \rightarrow L + d$	7.6	MLCT
429.2	0.05	$123 \rightarrow 129$	$L + d_{vz} \rightarrow L + d_{vz}$	66.2	$128 \rightarrow 133$	$d_{xy} \rightarrow L + d$	21.2	π - π^* + MLCT
423.3	1.68	$123 { ightarrow} 130$	$L + d_{vz} \rightarrow L + d$	76.6	$128 \rightarrow 134$	$d_{xy} \rightarrow L + d$	10.3	π - π^* + MLCT
409.9	5.06	$125 \rightarrow 131$	$d_{vz} + L \rightarrow L$	69.2	$128 \rightarrow 133$	$d_{xy} \rightarrow L + d$	11.1	MLCT
407.0	24.93	$128 \rightarrow 134$	$d_{xy} \rightarrow L + d$	48.0	$124 \rightarrow 131$	$d_{xz} + L \rightarrow L$	15.1	MLCT
398.3	33.58	$128 \rightarrow 133$	$d_{xy} \rightarrow L + d$	31.4	$127 \rightarrow 134$	$d_{vz} \rightarrow L + d$	16.3	MLCT
396.6	3.4	$124 \rightarrow 131$	$d_{xz} + L \rightarrow L$	43.0	$127 \rightarrow 133$	$d_{vz} \rightarrow L + d$	22.8	MLCT
392.4	40.26	$126 \rightarrow 134$	$d_{xz} \rightarrow L + d$	42.0	$124 \rightarrow 131$	$d_{xz} + L \rightarrow L$	19.3	MLCT
390.3	14.54	$124 \rightarrow 132$	$d_{xz} + L \rightarrow L$	24.5	$126 \rightarrow 133$	$d_{xz} \rightarrow L + d$	20.4	MLCT
387.8	14.32	$125 \rightarrow 132$	$d_{yz} + L \rightarrow L$	66.6	$124 \rightarrow 131$	$d_{xz}+L\rightarrow L$	10.0	MLCT
377.2	64.93	$124 \rightarrow 132$	$d_{xz} + L \rightarrow L$	45.6	$127 \rightarrow 134$	$d_{yz} \rightarrow L + d$	8.6	MLCT
370.2	83.99	$126 \rightarrow 134$	$d_{xz} \to L + d$	25.5	$128 \rightarrow 134$	$d_{xy} \rightarrow L + d$	18.7	MLCT
358.8	18.31	$122 \rightarrow 130$	$L + d_{xy} \rightarrow L + d$	53.0	$127 \rightarrow 134$	$d_{yz} \rightarrow L + d$	17.8	π - π^* + MLCT
353.8	1.15	$124 \rightarrow 133$	$d_{xz} + L \rightarrow L + d$	17.7	$128 \rightarrow 139$	$d_{xy} \rightarrow d_{z^2}$	13.2	MLCT + d-d
353.2	42.76	$122 \rightarrow 129$	$L + d_{xy} \rightarrow L + d_{yz}$	70.8	$126 \rightarrow 134$	$d_{xz} \rightarrow L + d$	7.6	π - π^* + MLCT
348.4	79.38	$124 \rightarrow 134$	$d_{xz} + L \rightarrow L + d$	30.9	$125 \rightarrow 133$	$d_{yz} + L \rightarrow L + d$	19.5	MLCT
347.6	1.96	$123 \rightarrow 131$	$L + d_{yz} \rightarrow L$	87.8	$125 \rightarrow 134$	$d_{yz}+L\rightarrow L+d$	3.6	π - π^* + MLCT
341.9	30.92	$125 \rightarrow 138$	$d_{yz} + L \rightarrow d_{z^2} + L$	17.3	$126 \rightarrow 133$	$d_{xz} \rightarrow L + d$	12.8	d-d + MLCT
337.3	68.5	$127 \rightarrow 134$	$d_{yz} \rightarrow L + d$	17.1	$125 \rightarrow 134$	$d_{yz}+L\rightarrow L+d$	17.0	MLCT
334.8	7.11	$123 { ightarrow} 132$	$L + d_{yz} \rightarrow L$	47.1	$125 \rightarrow 133$	$d_{yz}+L\rightarrow L+d$	11.0	π - π^* + MLCT
332.2	23.25	$123 { ightarrow} 132$	$L + d_{yz} \rightarrow L$	27.8	$124 \rightarrow 133$	$d_{xz} + L \rightarrow L + d$	14.1	π - π^* + MLCT
331.9	31.33	$124 \rightarrow 133$	$d_{xz} + L \rightarrow L + d$	19.8	$123 \rightarrow 132$	$L + d_{yz} \rightarrow L$	15.5	MLCT + π - π^*
322.9	196.28	$124 \rightarrow 134$	$d_{xz} + L \rightarrow L + d$	39.7	$125 \rightarrow 133$	$d_{yz}+L\rightarrow L+d$	12.0	MLCT
315.9	1.87	$128 { ightarrow} 135$	$d_{xy} \rightarrow L + d$	42.4	$125 \rightarrow 134$	$d_{yz}+L\rightarrow L+d$	18.2	MLCT
305.9	4.35	$123 \rightarrow 133$	$L + d_{yz} \rightarrow L + d$	79.5	$128 \rightarrow 136$	$d_{xy} \rightarrow d_{x^2-v^2}$	7.3	π - π^* + d-d
305.5	11.29	$128 \rightarrow 135$	$d_{xy} \rightarrow L + d$	41.3	$126 \rightarrow 135$	$d_{xz} \rightarrow L + d$	20.0	MLCT
302.2	30.94	$128 \rightarrow 136$	$d_{xy} \rightarrow d_{y^2,y^2}$	69.4	$126 \rightarrow 136$	$d_{xz} \rightarrow d_{x^2,y^2}$	12.0	d-d
299.8	1.42	$123 \rightarrow 134$	$L + d_{vz} \rightarrow L + d$	82.7	126→135	$d_{xz} \rightarrow L + d$	8.3	π - π^* + MLCT
298.7	3.95	$122 \rightarrow 131$	$L + d_{xv} \rightarrow L$	85.6	$127 \rightarrow 135$	$d_{vz} \rightarrow L + d$	6.5	π - π^* + MLCT
294.2	78.02	$127 \rightarrow 135$	$d_{vz} \rightarrow L + d$	43.5	126→136	$d_{xz} \rightarrow d_{v^2 v^2}$	28.9	MLCT + d-d
293.7	18.39	$126 \rightarrow 135$	$d_{xz} \rightarrow L + d$	49.3	$127 \rightarrow 136$	$d_{yz} \rightarrow d_{2}^{x-y}$	27.3	MLCT + d-d
289.8	74.45	$122 \rightarrow 132$	$L + d_{xy} \rightarrow L$	44.4	121→129	$L \rightarrow L + d_{yz}$	10.9	π - π^*

Table S6 Excited states of the HS state of $[Fe(pypypyr)_2]$ as determined with TD-DFT. For each state, the wavelength λ , the intensity, the two excitations with the highest weight and the assigned type of transition are given. For each excitation, the two involved molecular orbitals and their respective assignments are given, as well as their weight.

			excitation 1			excitation 2		
λ/nm	intensity / a. u.	MO numbers	MO types	weight / %	MO numbers	MO types	weight / %	assignment
3410.1	0.07	$126\beta \rightarrow 133\beta$	$d_{xz} \rightarrow L + d_{xv}$	48.8	$126\beta \rightarrow 131\beta$	$d_{xz} \rightarrow L + d_{xv}$	35.0	MLCT
2817.9	0.73	126eta ightarrow 134eta	$d_{xz} ightarrow d_{yz}$ + Ľ	45.2	126eta ightarrow 132eta	$d_{xz} \rightarrow L + d_{yz}$	17.6	d-d + MLCT
862.8	10.53	126eta ightarrow 137eta	$d_{xz} \rightarrow \dot{L} + d$	44.0	126eta ightarrow 127eta	$d_{xz} \rightarrow L + d_{yz}$	39.2	MLCT
814.7	0.7	126eta ightarrow 138eta	$d_{xz} \rightarrow d_{z^2}$	35.8	126eta ightarrow 139eta	$d_{xz} \rightarrow L + d_{z^2}$	26.4	d-d + MLCT
732.6	13.45	126eta ightarrow 127eta	$d_{xz} \rightarrow L + d_{vz}$	45.0	126eta ightarrow 137eta	$\mathrm{d_{xz}} ightarrow \mathrm{L} + \mathrm{d}$	28.6	MLCT
701.4	7.21	126eta ightarrow 128eta	$d_{xz} \rightarrow L + d_{xz}$	79.7	126eta ightarrow 138eta	$d_{xz} \rightarrow d_{z^2}$	3.9	MLCT + d-d
627.8	1.4	125eta ightarrow 127eta	$L \rightarrow L + d_{yz}$	35.2	$130 \alpha \rightarrow 131 \alpha$	$L \rightarrow L^{-}$	18.5	π - π^*
625.1	2.35	124eta ightarrow 127eta	$L + d \rightarrow L + d_{yz}$	25.7	$130 \alpha ightarrow 132 lpha$	$L \rightarrow L$	21.5	π - π^*
565.5	2.32	126eta ightarrow 129eta	$d_{xz} \rightarrow d_{xy}$	69.7	124eta ightarrow 127eta	$L + d \rightarrow L + d_{yz}$	8.0	d-d + π - π^*
552.9	5.93	125eta ightarrow 127eta	$L \rightarrow L + d_{yz}$	47.2	$130 \alpha \rightarrow 131 \alpha$	$L \rightarrow L$	35.1	π - π^*
545.0	16.09	124eta ightarrow 127eta	$L + d \rightarrow L + d_{yz}$	44.1	$129\alpha \rightarrow 131\alpha$	$L \rightarrow L$	34.0	π - π^*
544.7	1.16	126eta ightarrow 130eta	$d_{xz} \rightarrow L + d_{yz}$	39.7	129lpha ightarrow 132 lpha	$L \rightarrow L$	21.0	MLCT + π - π^*
542.9	1.86	130 lpha ightarrow 132 lpha	$L \rightarrow L$	49.7	$129\alpha \rightarrow 131\alpha$	$L \rightarrow L$	25.8	π - π^*
541.5	0.74	129lpha ightarrow 132 lpha	$\mathrm{L} \to \mathrm{L}$	36.2	126eta ightarrow 130eta	$d_{xz} \rightarrow L + d_{yz}$	33.8	π - π^* + MLCT
530.6	22.63	125eta ightarrow 128eta	$L \rightarrow L + d_{xz}$	67.7	130 lpha ightarrow 132 lpha	$L \rightarrow L$	15.4	π - π^*
526.4	2.83	124eta ightarrow 128eta	$L + d \rightarrow L + d_{xz}$	56.2	129lpha ightarrow 132 lpha	$L \rightarrow L$	12.6	π - π^*
514.5	5.36	124eta ightarrow 128eta	$L + d \rightarrow L + d_{xz}$	22.5	125eta ightarrow 129eta	$L \to d_{xy}$	11.7	π - π^* + LMCT
514.2	2.35	124eta ightarrow 129eta	$L + d \rightarrow d_{xy}$	16.0	125eta ightarrow 131eta	$L \rightarrow L + d_{xy}$	15.9	LMCT + π - π^*
464.8	4.04	126eta ightarrow 131eta	$d_{xz} \rightarrow L + d_{xy}$	28.3	126eta ightarrow 133eta	$d_{xz} \rightarrow L + d_{xy}$	16.2	MLCT
462.7	2.51	$128 \alpha \rightarrow 131 \alpha$	$d_{x^2-v^2} \rightarrow L$	34.1	126eta ightarrow 131eta	$d_{xz} \rightarrow L + d_{xy}$	14.5	MLCT
459.3	4.88	$127 \alpha \rightarrow 131 \alpha$	$d_{z^2} \rightarrow L$	21.0	126eta ightarrow 132eta	$d_{xz} \rightarrow L + d_{vz}$	18.5	MLCT
458.5	9.27	126eta ightarrow 132eta	$d_{xz} \xrightarrow{z} L + d_{yz}$	38.6	$126\beta \rightarrow 134\beta$	$d_{xz} \rightarrow d_{vz} + L$	17.6	MLCT + d-d
434.9	2.75	$128\alpha \rightarrow 132\alpha$	$d_{v^2,v^2} \rightarrow L$	35.0	$127\alpha \rightarrow 132\alpha$	$d_{z^2} \rightarrow L$	23.3	MLCT
432.9	1.12	$127\alpha \rightarrow 131\alpha$	$\hat{d}_{a2} \rightarrow L$	39.6	$127\alpha \rightarrow 132\alpha$	$d_{r^2} \rightarrow L$	21.3	MLCT
423.7	6.05	$125\beta \rightarrow 129\beta$	$L \xrightarrow{z} d_{xy}$	22.9	$130 \alpha \rightarrow 133 \alpha$	$\stackrel{Z^-}{L} \rightarrow L$	19.3	LMCT + π - π^*
423.5	4.16	$130\alpha \rightarrow 133\alpha$	$L \rightarrow L$	33.2	$129\alpha \rightarrow 134\alpha$	$L \rightarrow L$	22.8	π - π^*
422.7	1.21	$130\alpha \rightarrow 134\alpha$	$L \rightarrow L$	41.5	$125\beta \rightarrow 129\beta$	$L \rightarrow d_{xv}$	24.5	π - π^* + LMCT
421.9	0.54	125eta ightarrow 130eta	$L \rightarrow L + d_{vz}$	68.6	$129\alpha \rightarrow 134\alpha$	$L \rightarrow L$	14.9	LMCT + π - π^*
421.3	1.85	$124\beta ightarrow 129\beta$	$L + d \rightarrow d_{xy}$	51.3	125eta ightarrow 131eta	$L \rightarrow L + d_{xv}$	39.1	LMCT + π - π^*
418.0	0.11	$124\beta \rightarrow 130\beta$	$L + d \rightarrow L + d_{vz}$	62.7	$124\beta \rightarrow 131\beta$	$L + d \rightarrow L + d_{xv}$	23.1	π - π^*
412.2	0.29	$123\beta \rightarrow 127\beta$	$L + d_{xz} \rightarrow L + \dot{d}_{vz}$	72.0	$124\beta \rightarrow 131\beta$	$L + d \rightarrow L + d_{xy}$	7.7	π - π^*
406.7	28.38	$129\alpha \rightarrow 134\alpha$	$L \rightarrow L$	39.6	$130\alpha \rightarrow 133\alpha$	$L \rightarrow L$	20.7	π - π^*
405.4	18.81	$129\alpha \rightarrow 133\alpha$	$\mathrm{L} \to \mathrm{L}$	24.0	$130 \alpha \rightarrow 134 \alpha$	$\mathrm{L} \to \mathrm{L}$	19.9	π - π^*
401.5	2.74	$126 \alpha \rightarrow 131 \alpha$	$L + d \rightarrow L$	70.0	$128 \alpha \rightarrow 131 \alpha$	$d_{v^2,v^2} \rightarrow L$	17.0	π - π^* + LMCT
397.3	2.04	$126\alpha \rightarrow 132\alpha$	$L+d\rightarrow L$	62.6	$128\alpha \rightarrow 132\alpha$	$d_{v^2 v^2} \rightarrow L$	14.1	π - π^* + LMCT
396.8	0.58	$125\alpha \rightarrow 131\alpha$	$L + d \rightarrow L$	59.2	$127\alpha \rightarrow 131\alpha$	$d_{2} \rightarrow L$	18.9	π - π^* + LMCT
394.8	0.96	$125\alpha \rightarrow 132\alpha$	$L + d \rightarrow L$	46.9	$127\alpha \rightarrow 132\alpha$	$d_2 \rightarrow L$	17.7	π - π^* + LMCT
393.3	3.03	$123\beta \rightarrow 128\beta$	$L + d_{yg} \rightarrow L + d_{yg}$	36.3	$125\alpha \rightarrow 132\alpha$	$L + d \rightarrow L$	15.7	π - π^*
391.6	7.09	$125\beta \rightarrow 132\beta$	$L \rightarrow L + d_{yz}$	62.1	$124\beta \rightarrow 131\beta$	$L + d \rightarrow L + d_{wv}$	11.3	π - π^*
390.0	9.88	$124\beta \rightarrow 132\beta$	$L + d \rightarrow L + d_{yz}$	39.1	$123\beta \rightarrow 128\beta$	$L + d_{y_7} \rightarrow L + d_{y_7}$	35.5	π - π^*
386.6	10.85	$122\beta \rightarrow 127\beta$	$L + d_{yy} \rightarrow L + d_{yz}$	59.3	$124\beta \rightarrow 132\beta$	$I_1 + d \rightarrow I_1 + d_{w_2}$	18.6	π - π^*
371.1	1.32	$122\beta \rightarrow 128\beta$	$L + d_{yy} \rightarrow L + d_{yz}$	55.5	$123\beta \rightarrow 129\beta$	$I_1 + d_{y_7} \rightarrow d_{y_7}$	11.9	π - π^* + LMCT
370.5	0.05	$122\beta \rightarrow 128\beta$	$L + d_{xy} \rightarrow L + d_{xz}$	37.9	$123\beta \rightarrow 129\beta$	$L + d_{xz} \rightarrow d_{xy}$ L + $d_{yz} \rightarrow d_{yy}$	13.2	π - π^* + LMCT
369.1	0.24	$127\alpha \rightarrow 133\alpha$	$d_2 \rightarrow I_1$	21.4	$123\beta \rightarrow 131\beta$	$L + d_{yz} \rightarrow L + d_{yy}$	19.3	$MLCT + \pi - \pi^*$
365.6	6.21	$129\alpha \rightarrow 135\alpha$	$I_z \rightarrow I_z$	43.7	$130\alpha \rightarrow 136\alpha$	$L \to L$	36.3	π - π^*
365.5	14.82	$130\alpha \rightarrow 135\alpha$	$L \rightarrow L$	45.9	$129\alpha \rightarrow 136\alpha$	$L \rightarrow L$	32.8	π - π^*
362.9	31.18	$128\alpha \rightarrow 133\alpha$	$d_2 \rightarrow I$.	29.3	$126\alpha \rightarrow 133\alpha$	$L + d \rightarrow L$	15.1	$MLCT + \pi - \pi^*$
362.3	97.8	$125\beta \rightarrow 133\beta$	$I \rightarrow I + d_{-}$	17.3	$130\alpha \rightarrow 136\alpha$	$I \rightarrow I$	15.5	$\pi_{-}\pi^{*}$
359.9	83 43	$120\rho \rightarrow 130\rho$ $129\alpha \rightarrow 136\alpha$	$I \rightarrow I$	21.1	$124\beta \rightarrow 133\beta$	$I + d \rightarrow I + d_{-}$	15.0	$\pi_{-}\pi^{*}$
358.3	4 97	$129\alpha \rightarrow 134\alpha$	d a a \rightarrow I	32.0	$127\alpha \rightarrow 132\alpha$	$d_{a} \rightarrow I$	20.4	MICT
550.5	7.4/	1200 -713 4 0	$u_{x^2-y^2} \rightarrow L$	52.0	12/u 7155U	$u_{z^2} \rightarrow L$	20.4	IVILUI

S3.6 Additional NEXAFS spectra and data evaluation

Due to thermal expansion the absolute position of the measurement beam on the sample changes slightly during heating and cooling experiments. In the case of bulk experiments, a non-uniform distribution of the sample on the substrate, i.e., different sample thicknesses and topologies, is to be expected. As a result, the bulk spectra during cooling and heating cycles differ in intensities, which limits their comparability. To address this, all spectra were rescaled so that the area below the curves is identical in all cases (see Fig. S17a).

For the determination of the relative HS fractions, a linear combination of two reference spectra was used. The two template spectra are the spectrum with the highest HS fraction (8 K, constant illumination, after cooling down from 100 K under constant illumination) and the spectrum with the lowest HS fraction (300 K, in darkness, before cooling down). A least-squares method under a program written in Mathematica²⁵ was employed using the reference spectra and some additional parameters (slope, offset, shift, scaling parameters) to obtain a fit function describing the experimental data and the HS fraction γ_{HS} of any given spectrum.

For the estimation of the maximum absolute HS fraction observed under constant illumination at 8 K after cooling down from 100 K, the spectrum was compared to spectra of the fully switching Fe(II) SCO compound $[Fe(H_2B(pz)_2)_2(bipy)]$ (see Fig. S17b) published previously.^{26,27} The two reference spectra were measured on 0.8 ML of the complex deposited on HOPG at 5 K in darkness (LS) or under constant illumination with 520 nm (HS). Using these two spectra directly to fit the spectra of $[Fe(pypypyr)_2]$ with the above-described least-squares method led to unsatisfying results. Instead, we fitted both reference spectra with two Gaussian functions each (see Eq. S13, Fig. S17c). To better fit the spectral shape of the NEXAFS spectra of $[Fe(pypypyr)_2]$, the Gaussian fits were shifted to lower energies and broadened (see Eq. S14). Finally, the maximum absolute HS fraction was estimated by a linear combination of the shifted Gaussian functions representing the LS and the HS spectrum (see Eq. S15, Fig. S17d) as $\gamma_{HS} \approx 48$ %.

$$I_{\text{Gauss}} = 1 + A_1 \cdot exp(-\frac{E - E_{c1}}{w_1}) + A_2 \cdot exp(-\frac{E - E_{c2}}{w_2})$$
(S13)

$$I_{\text{shifted}} = 1 + A_1 \cdot exp(-\frac{E - E_{\text{c1}} - E_{\text{sh1}}}{w_1 + w_0}) + A_2 \cdot exp(-\frac{E - E_{\text{c2}} - E_{\text{sh2}}}{w_2 + w_0})$$
(S14)

$$I_{\exp} = \gamma_{HS} \cdot I_{\text{shifted},HS} + (1 - \gamma_{HS}) \cdot I_{\text{shifted},LS}$$
(S15)

For presentational purposes, the raw data were smoothened using a LOESS regression (comparison of raw and smoothened data, see Fig. S18). The regression was performed in Origin⁸, setting the data area to 0.1. The different exponential fits of the LIESST excitation data are as follows:

$$\gamma_{\rm HS,exc.} = \gamma_{\rm HS,\infty} - (A_1 \cdot e^{-t/t_1} + A_2 \cdot e^{-t/t_2} + A_3 \cdot e^{-t/t_3})$$
(S16)

$$\gamma_{\rm HS,mono} = 0.841 - (0.202 \cdot e^{t/(0.052 \text{ min})}) \tag{S17}$$

$$\gamma_{\rm HS,bi} = 0.879 - (0.162 \cdot e^{t/(0.015 \text{ min})} + 0.010 \cdot e^{t/(0.943 \text{ min})})$$
(S18)

$$\gamma_{\rm HS,tri} = 0.888 - (0.135 \cdot e^{t/(0.011 \text{ min})} + 0.051 \cdot e^{t/(0.115 \text{ min})} + 0.086 \cdot e^{t/(1.661 \text{ min})})$$
(S19)

The initially accelerated isothermal relaxation at 8 K that dominates the low-temperature region (see Fig S13b) was obtained fitting the data in Fig. S20 with mono- and biexponential fits:

$$\gamma_{\rm HS, relax.} = A_1 \cdot e^{-t/t_1} + A_2 \cdot e^{-t/t_2}$$
(S20)

$$\gamma_{\rm HS,mono} = 0.985 \cdot e^{-t/(292.996 \text{ min})}$$
 (S21)

$$\gamma_{\rm HS,bi} = 0.913 \cdot e^{-t/(1289.940 \text{ min})} + 0.087 \cdot e^{-t/(11.910 \text{ min})}$$
(S22)

Once more, an imaginary data point was necessary to force asymptotic behaviour and the monoexponential fit poorly describes the data whereas the biexponential fit gives a satisfactory result.

We determined the heat rate for each of the two temperature-dependent NEXAFS experiments (see Fig. S21a; cooling under constant illumination: Eq. S23; heating in darkness: Eq. S24) by plotting the time that had passed since the beginning of the experiment (start of the last measurement before starting to heat or cool) against the temperature of the various data points.

$$t_{\text{CI},\downarrow} = \theta^{-1} \cdot (T - T_0) = -1.794 \text{ min/K} \cdot (T - 100 \text{ K})$$
(S23)

$$t_{\text{dark},\uparrow} = \theta^{-1} \cdot (T - T_0) = 0.853 \text{ min/K} \cdot (T - 8 \text{ K})$$
(S24)



Fig. S17 a) NEXAFS spectra of $[Fe(pypypyr)_2]$ powder pressed onto indium foil at 100 K (black) and at 8 K under constant illumination with a wavelength of 520 nm (red). The intensities of the two spectra differ vastly due to a change in the beam position upon temperature change. Thus, the spectra were corrected by rescaling them with the resulting spectra all having the same peak area (blue). b) NEXAFS spectra of $[Fe(H_2B(pz)_2)_2(bipy)]$ at 8 K in darkness (blue) and under constant illumination with a wavelength of 520 nm (red), representing the LS and HS spectra, respectively, of a fully switching Fe(II) SCO complex. c) Fit of the LS and HS (offset for better visibility) spectra of $[Fe(H_2B(pz)_2)_2(bipy)]$ using two Gaussian functions each (see Eq. S13). Fit parameters LS: $A_1 = 0.006$; $E_{c1} = 707.24$ eV; $w_1 = 0.553$ eV; $A_2 = 0.132$; $E_{c2} = 709.28$ eV; $w_2 = 0.731$ eV. Fit parameters HS: $A_1 = 0.107$; $E_{c1} = 707.88$ eV; $w_1 = 0.594$ eV; $A_2 = 0.105$; $E_{c2} = 708.61$ eV; $w_2 = 1.075$ eV. d) Fit of the NEXAFS spectra of $[Fe(pypypyr)_2]$ at 100 K and at 8 K under constant illumination using Eq. S15 with the shifted Gaussian functions from panel c (according to Eq. S14) to determine HS fractions of 1 % and 48 %, respectively. Shifting parameters at 100 K: $E_{sh1} = 1.19$ eV; $E_{sh2} = 0.75$ eV; $w_0 = 0.295$ eV. Shifting parameters at 8 K: $E_{sh1} = 0.86$ eV; $E_{sh2} = 0.78$ eV; $w_0 = 0.355$ eV.



Fig. S18 a) NEXAFS spectra of $[Fe(pypypr)_2]$ at 300 K in darkness as well as during cooling from 100 K to 8 K under constant illumination with 520 nm as measured without any smoothening. b) Comparison of the measured (coloured lines) and smoothened (LOESS regression) spectra (black lines) at 300 K, 100 K and 8 K. The spectrum at 300 K is set off to increase visibility. The spectrum at 80 K and, to a minor extent also the one at 90 K, show a distortion in the photon energy range 702-707 eV which is not removed by the smoothening. This is caused by a shift in the position of the measument beam on the sample due to thermal expansion. As a result, the overall intensity of the spectra drastically decreased from 100 K to 80 K (corrected by rescaling) before the beam was readjusted at 70 K. Consequently, noise has a higher impact on these spectra with low intensity. While, this does not play a role in the fit to the template spectra for the determination of γ_{HS} , these two data points were not used in the further analysis.



Fig. S19 a) NEXAFS spectra of $[Fe(pypypyr)_2]$ at 300 K in darkness as well as during the excitation at 8 K. The grey spectra were measured in darkness. Thus, the change in the spectral shape is probably caused by the SOXIESST effect. Illuminating with 520 nm led to a further increase in the intensity of the feature at 706.8 eV and a decrease in the intensity of the feature at 708.5 eV, which can in turn be attributed to the LIESST effect. b) Plot of the extracted HS fractions at 300 K (blue), upon reaching 8 K and after 6.5 min in darkness at that temperature (red), after several short intervals of illumination (black, cumulative irradiation time is given) and during constant irradiation with 520 nm (green). Fitting the cumulative irradiation interval data with a monoexponential function (black) yields poor results, whereas bi- (red) and triexponential (green) fits describe the data well (adjusted R² values are given as a measure of the fit quality). The inlay shows the magnified LIESST region.



Fig. S20 a) NEXAFS spectra during isothermal relaxation at 8 K in darkness after illumination with 520 nm. b) Extracted HS fraction from the experiments in panel a, relative to the highest observed fraction. The data were fitted using a mono- (black line) and a biexponential fit (red line). The former is a poor fit for the data. Both fits include an imaginary data point at 10000 min (0 % HS), to force asymptotic behaviour. No triexponential fit is given as there are too few data points for obtaining a meaningful fit.



Fig. S21 a) Plot of the time that has passed since the start of the experiment against temperature for both temperature-dependent NEXAFS spectroscopic experiments. Linear fits give information about the respective heat rates. b) NEXAFS spectra during heating in darkness. The extracted HS fractions are shown in Fig. 5d.

S3.7 Coordinates of DFT-calculated structures

Table S7 Atomic coordinates of the DFT-calculated structures of $[Fe(pypypyr)_2]$ in its two spin states

		[Fo(pypypyr)]][S			[Eq(pupupur)] UC	
		[re(pypypy1) ₂] LS	~	I	[re(pypypy1) ₂] HS	~
	X	y	2	λ	y	2
Fe	6.56041981341946	7.59511110339998	14.364115/2494/26	6.86226290902874	4.27756309948658	6.31951543208300
N	5.08299740561436	7.83723594423452	13.08852806304649	4.74427416013634	5.01935146/53691	5.7/11117/943231
N	5.37569480882297	8.210066/9043328	15.831629/4662866	5.4182/899215843	2.82170883179169	7.01882308661614
Ν	6.03202096145283	5.89677781017478	15.06974652519426	6.56717326318073	5.43839402357120	8.28909864174416
Ν	7.08714080748593	9.28854405041305	13.64381439667777	7.51751107911490	4.27973237795931	4.32628006703508
Ν	7.55734210280505	6.44261346340872	13.11876151527165	7.58495653000101	6.30011939524948	6.04124673071245
Ν	8.22969641280764	7.88299841742721	15.39964927960824	8.06302642340554	2.79258916539993	7.18697350004723
С	8.80844644000786	5.27545168368960	11.63722873922620	5.06553847279410	0.78122892618923	8.21785506124118
С	7.40780956043573	5.08970570353020	13.38681533185290	3.22237869684854	6.47920600737520	4.63294569780856
С	6.53111037995907	4.77803618104238	14.47119561985838	5.94143826593047	1.75185954353884	7.67084317177015
С	8.18133891530498	4.33928845896800	12.47351168852543	3.72090249631702	4.21349643222753	6.12121507810718
С	8.39047960143647	6.55625038154693	12.07460687160263	2.40128624744844	4.51571895801670	5.75247891535591
С	5.15766480469071	9.03013451258565	12.38401546643078	3.18349178324926	2.07466228442827	7.40505230615921
С	3.30956377369696	7.95429160958308	11.68750957438127	3.69625597953759	0.95432020619368	8.08150464629670
С	4.05918287462710	9.12580170384369	11.50069842710235	4.09744523047698	2.99289466154880	6.87925210583468
С	5.17375065413921	5.85301718072643	16.10219849586828	6.35652654911669	6.94882144366676	10.61382840560284
С	4.78712813542831	7.20638083767368	16.54248264796592	8.43875672433928	8.86284338981255	5.50881547347365
С	5.07879040438670	9.48262152566226	16.12810979467589	7.37311658020796	1.73639072370058	7.75456616002156
С	6.29473397656830	9.84223173263393	12.68253607660233	4.50395790638552	6.11315794963938	5.04419574805718
С	8.22379242636613	9.86084137388835	14.07383720506130	2.15050377392837	5.66216195601623	5.00135944544466
С	8.89469319829038	9.03322155544701	15.09383424005679	9.56565233537795	1.34829661163047	8.08758331959267
С	8.76726062680933	7.03241126066269	16.28433453361826	6.09427030476116	4.89202725507343	9.41179285850934
С	3.98275223300654	7.19307956981674	12.67415028019327	6.96214118548190	6.72804055232013	8.28921420052962
С	6.13598107490695	3.51644130656881	14.97439867198365	7.51404267917403	7.22844151625142	7.00401000416572
С	4.74742534794620	4.63205988327000	16.63269567836300	8.05611651684390	6.58326971845777	4.79982789285367
С	3.89417122621140	7.48424752892132	17.58306647954155	8.01708638670515	5.48822252766753	3.87460901150261
С	4.19627383195792	9.82894963606691	17.14875241214353	7.56730037611299	3.42228342895060	3.28878238899842
С	6.68187988234996	11.08564772663523	12.12998590094961	9.37420164396025	2.55711485406646	7.38583739159882
С	8.65250910259869	11.08714123859861	13.55795853909180	8.28407177594007	0.82206957853316	8.32506968828633
С	10.11425093647233	9.34779255808764	15.70308081795496	5.96785917199497	5.60666243764660	10.60294775613793
С	10.66463232081569	8.46407012585198	16.62966853028639	6.86227996133721	7.51603734610671	9.44595099805703
С	7.85259074383548	11.69266352153168	12.57256526953894	7.93311294077287	8.54344668231424	6.78091311186296
С	3.59461849498928	8.80958316977347	17.89272956284691	8.50503886558518	7.89728717840684	4.51551845145370
С	5.25082235915336	3.45747133486856	16.04591871608568	8.38427785768741	5.37615687191596	2.51657791179037
С	9.97959574605645	7.28143763850659	16.92344619440633	8.09622601765286	4.05235344527775	2.14251539885346
Н	8.65499730486339	7.53334748162290	11.66874202682581	8.88984363796000	8.13367932380180	3.52261828380716
Н	9.48124310245816	5.06629886342518	10.80613144818910	8.80900777314111	6.15890691007171	1.88869765623415
Н	8.26591157978811	3.25377183868231	12.43078072117987	8.25357700872862	3.59630370889721	1.16562224021729
Н	5.56690194982787	10.24266344735803	15.51470641843180	10.52010042386808	0.91036894392183	8.37794067280799
Н	10.62772925303918	10.27381095315155	15.44208207425151	6.27251255444205	7.54650965802817	11.52474903000898
Н	10.37754044784734	6.55395024043735	17.63311292099991	8.77762880834669	9.88121027741395	5.30193577081643
Н	3.84515846642013	9.94398751472468	10.81370141198824	7.18453206939390	8.55714641857210	9.43389397409524
Н	2.39115461216703	7.67344591107200	11.17324104373938	7.86951897280228	9.30292149169286	7.55942733189288
Н	4.93869754457283	2.48536218726929	16.43576242913286	10.12980171030987	3.25095257995068	7.01438378051945
Н	2.89708593121823	9.04467209189025	18.69986465366945	8.04041809904567	-0.10814460221701	8.83757662137182
Н	8.15814641958725	12.65123301256015	12.14605639856605	3.07427236620576	7.38122827943191	4.03650740073488
Н	11.61888150385990	8.69048595025687	17.11033419273799	5.57521267354530	5.11797914751893	11.49643870791467
Н	9.57473893318824	11.55643846677484	13.90020873293284	7,23362711894559	2.38946645781485	3.39939184447112
Н	3,43641503520150	6.66421996761910	18,13747036551852	1.12998999275673	5.91006598830537	4.69951600025576
Н	3.98501126753244	10.88089832869107	17.34878779993676	5.80767602508707	3.83962246414061	9.35258361134783
Н	6.06325491452162	11.54859121764525	11.35969650997593	5.37481021118039	6.71619618654158	4.77806392602253
н	8.20166808957667	6.11791147506878	16.47290078778720	5.47661070387203	-0.08278544351522	8.74168475108562
Н	3.71495468504532	6.21697017891111	13.08015214473090	1.58378560348314	3.85297465362371	6.03598681627057
Н	6.52306220762131	2.60721694265502	14.51192747010215	3.00953787998895	0.21681502786653	8.50463505790192
Н	4.04937536680739	4.58827541071091	17.46886343171450	2.10826628390250	2.21719168017016	7.30284468518671

Table S8 Atomic coordinates of the DFT-calculated structures of $[{\sf Fe}({\sf terpy})_2]$ in its two spin states

		[Fe(terny)]]IS			[Fe(terny)] HS	
	r	v	7	ř	v	7
Fo	0.01056242251682	0.02050471587157	<u>~</u> 0.02403203605000	0.01700760535078	0.01703073171526	0.02850800004860
N	0.82602474225120	1 10671867068161	1.28813813776201	0.01344068707452	1 32064220008475	1 44035675738478
C	1 78077016882714	0.71/82021522222	2 00008076625728	1 85/08/00503357	0.84001634802176	2 27115000100067
c	0 41106262425767	2 47774422200452	1 33087018102020	0 52280823751222	2 61526650071022	1 47465440508812
C	0.00400075246007	2 26255011105122	2 25044566956009	1 00680770064708	2 50651694472575	2 20000120870812
C	1 09500640792575	-3.303330 444 93433 9.00757199917044	2 11212142227520	-1.09080779904708	2 02022224002416	2.39099139879819
C	2 20017201104402	1 55208400580070	2 02002480075412	2.0/33/033303/13	1 69776200572400	2 21521828700061
C	2.3991/291194403	0.71270429060055	1 9525024009/3413	-2.40223028210874	-1.08//02003/2400	-3.21321828700001
N	1 20527064215259	1 26252470575002	-1.03230220000/29	1 45721510045190	1 22070762251951	1 12466700102050
C	2 01280078708062	1.20332479373002	2 5/8380801103//	2 15/036113/2018	1.23079702331031	2 82587565545524
c	1 47205264041770	2 55608555307182	0 55704771588264	1 68750/07555188	2 52446865013106	0.88727076217734
c	2 18440286600747	2.33000333337102	2 22256818852175	2 202/876/850/22	2.52440605015190	2 56753185288606
c	2 40077722680521	2.81300990433137	1 20061/26208537	2 65008000161106	2.01490033419407	1 57820180562455
c	0.64008825065806	2 7626446000265	0 35530784676038	0.52875707157440	2 075327/36738/0	0 /87/5/80753132
N	1 00160801044063	1 68850814664810	0.0000000000000000000000000000000000000	0.03287006604308	1 07303868083802	0 2260/202101822
C	1 26207175628755	4 00620400863642	0.10028236804722	1 08/05362620283	4 25538588037617	0.32004292101032
c	2 25065307203862	4 15154753200657	0.77753456104144	2 07731144601201	4 40365814508825	0 56580360504044
c	2.23703377273002	3 04604022062671	1 55322600670555	2.07731144001201	3 44011123120266	1 20527840506214
c	1 057//10318/200	1 83382285000202	1.33364344703727	1 885/2277182025	2 201/2000250778	1.373276852255066
ц	0.06015534850014	4 85301814734517	0.81086432020288	0.75507641107113	5 06106653558018	1.0/32080500/003
н	2 75106234325360	-5 11548232710821	0.02104007686166	2 52270433438828	-5.00100055556018	0 65717253030603
н	3 38536803201677	-3 11508987501450	2 32092107374054	3 26234388366297	-3 59531584272406	2 15247098189845
н	2 20779871235864	-0.94832426683959	1 92083610164684	2 17015514172319	-1 35416558143430	1 86775831415028
н	-0 66059256659297	-4 40312538089601	-2 31509946460434	-0 79454594993523	-4 55261829323104	-2 42820959183089
н	-2 44699528192109	-3 56058361200713	-3 83786024634155	-2 53404537159043	-3 70268940547139	-3 99213481976432
н	-3 17051804010217	-1 18019772370480	-3 70296376009510	-3 22362108162475	-1 31268049220560	-3 80855174338242
н	-3 61248675209833	1 01031665672188	-3 33653926130088	-3 73002451657988	0 74583837633646	-3 59270510616550
н	-3 91909085068453	3 42346370640263	-2 75597910865697	-4 15460736704889	3 15583952600438	-3 13441535423019
н	-2 50099308279669	4 41717626189960	-0 92334499483282	-2.80764767430837	4 31600476844352	-1 34624800878878
н	-0.84132452603096	2 95486556087610	0 23906197879278	-1 07426313188416	2 98821755221749	-0 10932846244180
N	-1.25587649724436	-0.31916553280658	1.52045421909609	-1.21702631759584	-0.23601711177017	1.80548071499431
N	0.79449160695557	1.15287899603198	1.23771014495643	0.89215072923394	1.28751729838521	1.38207151003332
N	1.48083366623384	0.65951278656128	-1.15874911290843	1.66430935432665	0.90678791104946	-1.10910351942499
С	2.29227736534417	1.55261353881321	-0.52380844876539	2.41861795139264	1.76921639661020	-0.38932636488721
Ĉ	1.89501649859894	1.83822912199921	0.86873234180291	1.97629645080449	1.99148344253746	1.01370286919018
Ĉ	0.25581281072145	1.25735312095362	2.46855371108406	0.37534618543332	1.37105408104025	2.61959043785881
C	-0.93842551738259	0.40530548322118	2.63079434981242	-0.82604662322533	0.52542263900506	2.85336675406469
С	-2.32196949721676	-1.12893048508284	1.55476907538665	-2.29478080535918	-1.01917657262579	1.91969183438608
С	-3.12655125577012	-1.26358874023675	2.68663701074873	-3.04889834519555	-1.09236856082041	3.09145829441648
С	-2.81056363011098	-0.52517947650394	3.82815625448114	-2.65338639033977	-0.31581239992394	4.18213591082111
С	-1.70079309108731	0.32145934217172	3.79810879721971	-1.52882173097219	0.50352649799431	4.06306476402320
С	0.83804820836975	2.10301847191196	3.41899167959565	0.96182812381485	2.20793816813779	3.57782996970987
С	1.98063745432219	2.82609879791224	3.06020181687307	2.08637752873904	2.95286486552274	3.21565344319749
С	2.52172559716020	2.69892629527288	1.77637510643332	2.60567218304884	2.85129449336205	1.92294494698973
С	3.39204279937192	2.12406991070104	-1.16808635112444	3.53822488914742	2.39113355444882	-0.95287929262976
С	3.66598476953773	1.77183981657887	-2.49110368182706	3.87960468735892	2.10783899730009	-2.27712776017655
С	2.82869585930464	0.85768267141816	-3.13246531945820	3.09489703870458	1.21293665387712	-3.00661649667393
С	1.74749647877598	0.32688880598323	-2.42820333948927	1.99170842445934	0.63591755843865	-2.37667683455955
Η	-2.53995661811230	-1.68905578932924	0.64354254791015	-2.56066758297728	-1.61319360029990	1.04074963200167
Η	-3.98506640129811	-1.93724289945978	2.66579847989187	-3.92196061965215	-1.74517033469637	3.14457966935206
Η	-3.41921951267004	-0.60527214694134	4.73134804327352	-3.21401461461856	-0.34483544198012	5.11907839049095
Н	-1.43211753100532	0.91045597106587	4.67556862633809	-1.21161643799085	1.11701055758166	4.90598931222900
Η	0.41564537045605	2.19933599606919	4.41937301204456	0.55769428060042	2.28382893061455	4.58673639428268
Н	4.02945125127188	2.83657948359022	-0.64319297112102	4.14408826502565	3.08662244325404	-0.37202883199480
Η	4.52145192565864	2.20624295394969	-3.01265823456924	4.75098701803367	2.58319615412293	-2.73290970875929
Η	3.00469311056423	0.55488061685746	-4.16605507603198	3.32780252105479	0.96634850965341	-4.04387024406405
Η	1.07126932468549	-0.38990804448654	-2.89790310304610	1.34238287845758	-0.06579925443697	-2.90820435227918
Н	2.45229525779161	3.49195571496550	3.78574598465678	2.56005519784325	3.61456943374053	3.94395068191099
H	3.41282180885153	3.26055324963327	1.49482676906815	3.48258054175347	3.43224876535868	1.63875411130030

Table S9 Atomic coordinates of the DFT-calculated structure of $[{\rm Zn}({\rm pypypyr})_2]$

	x	у	Z		x	у	Z
С	3.19744979147009	2.05703808779560	7.27547683226994	С	8.25632769791301	0.94129643240682	8.49766001204688
С	3.70417479091429	0.97165219502787	8.01397155992403	Н	5.30186017450918	6.80564111722406	4.79518114844623
С	4.11248065684193	2.97527080793378	6.75524209672580	С	3.18266589314388	6.43720898044702	4.48301125015587
Η	2.12443404511525	2.17709811350023	7.13179594506909	Н	1.13941746564466	5.72132967633530	4.36476456128259
Ν	5.42798206998176	2.83414914299899	6.95159631398548	Н	5.82220978263380	3.84137424122189	9.44142853749537
С	3.72145319607771	4.17627143783975	5.96158035362550	С	6.13105673844224	5.57937299782811	10.71001037049116
Η	3.01487502681847	0.23577619246270	8.43583081834699	С	7.09914526544209	7.44708938916894	9.54031851544610
С	5.06710021289633	0.83613178374365	8.21640827423163	С	8.02485066770336	8.48190428698482	6.83386524455995
Zn	6.90957659883146	4.24310660472691	6.29821710982816	С	8.45015860314380	7.87409779051795	4.52644124632414
С	5.94639359580905	1.80770181624106	7.66983664933286	С	8.16809340755124	5.42320903798264	2.47871943739725
Ν	4.70572330257984	5.05198818968802	5.70373468249265	С	7.83483311374676	4.11993117385007	2.07774567375495
С	2.41613715192422	4.39101591966411	5.49148446429572	Н	7.01197347870995	2.42902247065655	3.32651295758287
Η	5.47306095374062	0.00353799717864	8.79221562280073	С	9.54198952094944	1.47750400650613	8.32426852161888
Ν	6.62975494963331	5.41219360901705	8.37553318336246	Η	10.14894418155260	3.35402330351391	7.22591193752131
Ν	7.61314983381483	6.25912221397988	6.07875202672230	Η	7.99209523995613	0.02615345961817	9.02671114372978
Ν	7.39055830123486	4.27876521288646	4.29721911180230	Н	3.01726537304041	7.34265672427705	3.89629485915140
Ν	8.08367066987111	2.86506121102015	7.27639455724338	Н	5.74400554858293	5.10413207921638	11.61319188041859
С	7.37155894371462	1.82186732078134	7.83514269875314	С	6.60598255686112	6.89267971633008	10.72081354330338
С	4.45277149894808	6.14317333304735	4.98452091380319	Н	7.48709500661392	8.46546592140578	9.53186477222284
С	2.14711466487323	5.53764253353468	4.74531220413528	Н	8.01257642644046	9.22985684453924	7.62566424131437
Η	1.62686886601285	3.66609187371375	5.69057846759091	С	8.45905747971834	8.81909110777112	5.53842753327454
С	6.16944270948264	4.87622712111909	9.50374436969681	Н	8.77421886998373	8.12495835763875	3.51564806793911
С	7.09748831311459	6.67049074501862	8.37081424788426	Н	8.56998006107711	6.22023141626358	1.85394924683974
С	7.60392262325690	7.16909861462118	7.05873356378486	Н	7.92417303285225	3.69608997155970	1.07806519521298
С	8.00107322604652	6.55839846048314	4.81489536711230	Η	10.48126634925060	1.06684081634300	8.69314014615332
С	7.88410563264685	5.49275733970820	3.86137727538318	Н	6.59894589302217	7.47980983341268	11.64247948965475
С	7.36300492346978	3.45782279300035	3.23325903063751	Н	8.79806758959230	9.83718352059308	5.33038967989933
С	9.37990803280077	2.65893465565421	7.56646304592129				

S3.8 Crystal structure data

CCDC-2233051 ([Fe(pypypyr)₂]) and CCDC-2233052 ([Zn(pypypyr)₂]) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for $C_{28}H_{20}FeN_6$ (M = 496.35 g/mol):

monoclinic, space group C2/c (no. 15), a = 28.5552(4) Å, b = 13.9204(2) Å, c = 16.0184(2) Å, $\beta = 103.054(2)^{\circ}$, $\alpha = \gamma = 90^{\circ}$, V = 6202.76(15) Å³, Z = 8, T = 99.99(10) K, μ (Cu K α) = 4.072 mm⁻¹, $D_{calc} = 1.063$ g/cm³, 41621 reflections measured (6.354° $\leq 2\Theta \leq 160.616^{\circ}$), 6703 unique ($R_{int} = 0.0326$, $R_{sigma} = 0.0146$) which were used in all calculations. The final R_1 was 0.0543 ($I > 2\sigma(I)$) and wR_2 was 0.1667 (all data).

Crystal Data for $C_{28}H_{20}N_6Zn \cdot DCM$ (M = 590.79 g/mol):

monoclinic, space group $P2_1/c$ (No. 14), a = 9.95270(10) Å, b = 13.24570(10) Å, c = 19.3402(2) Å, $\beta = 95.0880(10)^\circ$, $\alpha = \gamma = 90^\circ$, V = 2539.58(4) Å³, Z = 4, Z' = 1, T = 100.00(10) K, μ (Cu K α) = 3.533 mm⁻¹, 39393 reflections measured (8.1° $\leq 2\Theta \leq 159.942^\circ$), 5469 unique ($R_{int} = 0.0189$, $R_{sigma} = 0.0087$) which were used in all calculations. The final R_1 was 0.0390 ($I > 2\sigma(I)$) and wR_2 was 0.1114 (all data).



Fig. S22 Molecular structures of a) $[Fe(pypypyr)_2]$ and b) $[Zn(pypypyr)_2] \cdot DCM$ as found in the single-crystal structures. All atoms are numbered for reference in the tables in this subsection.

Table S10 Selected bond lengths r and	l angles α for the two complexes	$[M(pypypyr)_2]$ (with M = Fe,Zn)
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		r(Fe) / Å	r(Zn) / Å				$lpha$ (Fe) / $^{\circ}$	$\alpha(Zn)$ / $^{\circ}$
M1	N1	1.890(2)	2.3153(18)	N1	M1	N2	80.82(8)	71.43(7)
M1	N2	1.9759(17)	2.1218(17)	N1	M1	N3	81.18(8)	147.72(7)
M1	N3	1.966(2)	2.0707(18)	N1	M1	N21	179.13(8)	88.73(6)
M1	N21	1.880(2)	2.3733(18)	N1	M1	N22	99.10(8)	95.92(6)
M1	N22	1.9619(19)	2.1341(17)	N1	M1	N23	98.61(8)	88.92(6)
M1	N23	1.9642(18)	2.0776(18)	N2	M1	N3	162.00(9)	78.19(7)
				N2	M1	N21	100.03(8)	108.01(6)
				N2	M1	N22	91.34(7)	167.35(7)
				N2	M1	N23	89.79(7)	101.21(7)
				N3	M1	N21	97.97(8)	90.48(7)
				N3	M1	N22	91.84(8)	114.24(7)
				N3	M1	N23	92.55(8)	107.77(7)
				N21	M1	N22	81.10(9)	70.91(6)
				N21	M1	N23	81.21(8)	148.22(7)
				N22	M1	N23	162.21(10)	77.83(7)

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Table S11 Comparison of the distortion parameters Σ (deviation of the *cis*-N-Fe-N angles from a perfect octahedron) and Θ (measure for the trigonal distortion towards a trigonal prismatic coordination sphere) found for calculated and crystal structures of various complexes with the structures of [M(pypypyr)₂]. The differences in distortion between the two Fe(II) spin states and between Fe(II) HS and Zn(II) are also given. Most notably, the difference between Zn(II) and Fe(II) HS is often very small. However, $\Delta\Theta$ is a bit higher for [M(tren(6–Mepy)₃)₂] and very high in the calculated structures of [M(pypypyr)₂]

	Σ			ΔΣ		Θ			$\Delta \Theta$	
	Fe _{LS}	Fe _{HS}	Zn	Fe_{HS} - Fe_{LS}	Zn-Fe _{HS}	Fe _{LS}	Fe _{HS}	Zn	Fe_{HS} - Fe_{LS}	Zn-Fe _{HS}
[M(pypypyr) ₂] _{calc.} / °	79.4	143.0	149.2	63.6	6.2	256.3	527.7	479.8	271.4	-47.9
[M(pypypyr) ₂] _{cryst.} / °	77.3	-	141.7	-	-	255.5	-	484.5	-	-
$[M(H_2B(pz)(pypz))_2] / ^{\circ}$	47.4	79.9	92.1	39.6	5.1	149.1	264.2	298.1	140.4	8.6
$[M(H_2B(pz)_2)_2(phen)] / ^{\circ}$	35.1	42.0	38.8	6.9	-3.2	115.4	152.9	144.7	37.5	-8.2
$[M(tren(6-Mepy)_3)_2] / ^{\circ}$	83.8	111.0	104.1	27.2	-6.9	231.1	336.5	314.2	105.4	-22.3
[Fe(terpy) ₂] _{calc.} / °	76.7	135.4	-	58.7	-	248.6	432.4	-	183.8	-
[Fe(terpy) ₂] _{crvst.} / °	83.1	-	-	-	-	273.9	-	-	-	-
[Fe(bpp(COOH) ₂) ₂] _{cryst.} / °	88.1	152.8	-	64.7	-	297.1	565.0	-	267.1	-

Table S12 Comparison of the bite angles ε found for calculated and crystal structures of $[M(pypypyr)_2]$ with the Fe(II) complexes of terpy and a bpp derivative. The two bite angles to the two different outer N atoms (1,2) are given for both ligands (A,B) separately. Compared to the other complexes, the Fe(II) HS and Zn(II) structures of $[M(pypypyr)_2]$ show highly asymmetric bite angles

	LS				HS				
	$\mathcal{E}_{A,1}$	$\epsilon_{\mathrm{B},1}$	$\epsilon_{\rm A,2}$	$\varepsilon_{\mathrm{B,2}}$	$\epsilon_{\mathrm{A},1}$	$\epsilon_{\mathrm{B},1}$	$\epsilon_{\rm A,2}$	$\varepsilon_{\mathrm{B,2}}$	
[Fe(pypypyr) ₂] _{calc.} / °	80.6	80.6	81.6	81.6	71.6	71.6	77.0	77.0	
[Fe(pypypyr) ₂] _{cryst.} / °	80.9	81.1	81.2	81.2	-	-	-	-	
[Zn(pypypyr) ₂] _{calc.} / °	-	-	-	-	70.3	71.1	79.4	79.0	
[Zn(pypypyr) ₂] _{crvst.} / °	-	-	-	-	71.4	70.9	78.2	77.8	
[Fe(terpy) ₂] _{calc.} / °	81.1	81.1	81.1	81.1	75.0	75.0	75.0	75.0	
[Fe(terpy) ₂] _{cryst.} / °	80.5	80.8	80.6	80.4	-	-	-	-	
[Fe(bpp(COOH) ₂) ₂] _{cryst.} / °	80.3	80.2	80.3	80.3	73.1	74.0	74.3	73.9	

S3.8.1 Crystalline packing structures

Based on the dependency of the occurrence of the different species on the environment, it may be worth investigating the packing and cooperative effects found in the single-crystal structure. The Fe(II) LS structure consists of two different isomers with equal incidence: with one ligand fixed in position, the pyrrole of the other ligand faces in opposing directions in the two isomers. Two different isomers then form a dimer with T-shaped π - π interactions between the 4-position of the outer pyridine of one ligand and the pyrrole of the other ligand (see Fig. S23c, green dotted lines). These dimers are then interacting with two other rotated dimers, one on each side, through similar T-shaped π - π interactions between the 3-position of the outer pyridine and the pyrrole that are not part of the intradimer interactions (see Fig. S23c, red dotted lines). Furthermore, there is displaced parallel π - π interaction between the pyridine that is part of the intra-dimer interaction (see Fig. S23c, black dotted lines). Thus, strongly interacting 1D chains are formed that have little interaction with each other. However, this does not necessarily reflect the structural behaviour in the above experiments, since XRD showed that the single-crystal structure and the bulk material do not have the same structure (see Fig. S4a).

Similarly, the crystal structure of $[Zn(pypypr)_2] \cdot DCM$ also contains four different complexes: the same two isomers that are also found in the Fe(II) complex in two distinct orientations, each. However, in this structure, there are no notable interactions between different complexes. Instead, the solvent dichloromethane interacts strongly with hydrogen atoms or the aromatic π -systems, thereby acting as a link between multiple complexes. Still, due to the lack of interactions between the complexes, no dimers, chains or other structures are observed. The strong interaction with the solvent, which is firmly included in the crystal structure, may indicate why it had proven difficult to remove solvents or trace impurities in our attempts to obtain an analytically pure sample and why all our attempts to obtain a solvent-free crystal structure were unsuccessful.

Unfortunately, the fact that the crystal structures are different from the powder investigated with the various methods described in this study heavily hinders the interpretation of the unique properties of $[Fe(pypypyr)_2]$ based on observed cooperative effects. Thus, it is only speculation that, for example, the dimers may be a recurring motif in the bulk material and vacuum-deposited films. Consequently, comparison of the crystalline packing with $[Fe(terpy)_2]^{2+}$ as well as $[Fe(bpp)_2]^{2+}$ derivatives is equally problematic.

Cautiously assuming that the strongly interacting dimers are indeed a recurring motif in the bulk material *as synthesised* and in self-organised thin films upon resublimation, may serve as an explanation for the incomplete excitation observed in all experiments. Based on the highest obtained HS fractions slightly below 50 % (ca. 40 % and 48 % for UV/Vis and NEXAFS spectroscopy, respectively), it may be speculated that only one of the distinct isomers in a dimer can be excited, as recently found for a similar complex.²⁸

Furthermore, many $[Fe(bpp)_2]^{2+}$ complexes show strong interactions with solvents and counterions, very similar to the strong interactions found in the crystal structures discussed in this study. Among the derivatives that show a spin transition despite exceptionally high distortion parameters similar to $[Fe(pypypyr)_2]$, most are substituted with carbonyl groups that are designed to facilitate



Fig. S23 a) Selected section of the crystal structure found for $[Fe(pypypr)_2]$. Dimers of different isomers (identical isomers are labelled with the same letter A or B, respectively; different indices indicate a different orientation) are interacting with each other via T-shaped π - π interactions between the pyrrole of one ligand and the outer pyridine of another (green dotted lines). The other pyrrole and pyridine then form further T-shaped π - π interactions that connect one dimer with a slightly rotated and diagonally displaced neighbouring dimer (red dotted lines). Every second dimer is oriented in the same direction. Finally, there is a parallel-displaced π - π interaction between a pyridine and a pyrrole of neighbouring dimers (black dotted lines). b, c) Molecular structure of $[Zn(pypypr)_2]$ as calculated using DFT. The same structure is shown once along the x-axis (b) and once along the y-axis (c) to visualize the different distortion of the two ligands in the yz- and xz-plane, respectively (frontal view). Additionally, the structure is shown along the intersecting line of the two ligand planes (top view) to visualize the angle θ between them (b). Elements are colour-coded according to orange: Zn; blue: N; grey: C; white: H. In the frontal view, the pyrrole of the second ligand is located in the rear. In the top view, pyr and py indicate the location of the pyrrole and the outer pyridine, respectively, in both ligands. d) Unit cell of the crystal structure found for $[Zn(pypypyr)_2] \cdot DCM$. Intermolecular interactions are shown as dotted lines. Isomers are labelled using the same combination of letters and indices also used in panel a). e) A different view on the unit cell of $[Zn(pypypyr)_2] \cdot DCM$.

intermolecular interactions.^{29,30} This includes $[Fe(bpp(COOH)_2)_2](ClO_4)_2$, another complex that supersedes the behaviour expected for a complex based on tridentate ligands that should be part of the $T_0 = 200$ K family (see Fig. 8).

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