

Electronic Supplementary Information

From Six-coordinate to Eight-coordinate Iron(II) Complexes with Pyridyltriazolo-pyridine Frameworks

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Experimental Section

Synthesis of 3-(6-(5-bromopyrimidin-4-yl)pyridin-2-yl)-[1,2,3] triazolo [1,5-*a*] pyridine = L_{N3} (ptpp): At -40° C, butyl-lithium (5.1 mL, 6.6 mmol, 1.1 eq) in hexane (1.3M) was added drop-wise to a stirred solution of 3-(2-pyridyl)-[1,2,3]triazolo[1,5-*a*]pyridine^[7] (1.2 g, 6.0 mmol) in toluene (190 mL). After 30 minutes a solution of 5-bromopyrimidine (2.9 g, 18.2 mmol, 3eq) in toluene (20 mL) was added drop-wise to the reaction solution, and the final mixture was let to react during 2 hours. The solution was then allowed to reach room temperature. Next a solution of KMnO₄ (1 g, 6.6 mmol, 1.1 eq) in 100 ml of water and 50 ml of saturated aqueous solution of ammonium chloride were added. After 30 minutes the organic layer got separated and the aqueous layer extracted with dichloromethane (3 x 50 mL). The combined organic layers were dried over sodium sulphate, filtered, and evaporated. By ethyl acetate treatment a yellow solid was obtained and identified as 3-(6-(5-bromopyrimidin-4-yl)pyridin-2-yl)-[1,2,3]triazolo[1,5-*a*] pyridine L_{N3} (0.72g, 34%). Mp: 206-208° C. ¹H NMR (300 MHz, CDCl₃): δ = 9.24 (s, 1H), 9.05 (s, 1H), 8.85 (d, *J* = 9.0Hz, 1H), 8.79 (d, *J* = 7.0Hz, 1H), 8.54 (dd, *J* = 8.0, 0.9Hz, 1H), 8.01 (dd, *J* = 7.9, 7.9Hz, 1H), 7.81 (dd, *J* = 7.7, 1.0Hz, 1H), 7.41 (ddd, *J* = 9.0, 6.7, 0.9Hz 1H), 7.08 (ddd, *J* = 6.9, 6.9, 1.2 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ = 162.8 (C), 162.6 (C), 161.0 (CH), 156.8 (CH), 154.4 (C), 151.6 (C), 137.7 (CH), 132.3 (C), 126.9 (CH), 125.4 (CH), 122.7 (CH), 121.7 (CH), 121.6 (CH), 119.0 (C), 116.2 (CH). MS (EI): *m/z*(%) = 352 (9), 325 (40), 245 (100), 218 (23), 191 (16), 166 (9), 140 (9), 114 (8), 109 (13), 63 (14), 51 (11). HRMS for C₁₅H₉BrN₆: 352.0072, found: 352.0076. IR (neat, cm⁻¹): 3121, 3037, 1593, 1561, 1410, 1150, 1112, 1022, 820, 773, 693, 673. UV/Vis: 219 nm (logε = 3.14) 285 nm (logε = 2.93) and 323 nm (logε = 2.93). Emission at 482 nm (irradiation at 335 nm) EtOH 10⁻⁵ M.

Synthesis of [Fe(L_{N3}=ptpp)₂](CF₃SO₃)₂·2.5H₂O (2): Under an argon atmosphere, to an almost colourless solution of 1Fe^{II}/2CF₃SO₃⁻, prepared from FeSO₄·7H₂O (34.75 mg, 0.125 mmol) and K(CF₃SO₃) (47 mg, 0.25 mmol) in methanol (20 mL), a solution of the ligand L_{N3}=ptpp (88.3 mg, 0.25 mmol) in CH₂Cl₂ (20 mL) was added drop-wise under stirring. The resulting red-violet solution was also evaporated under an argon stream to yield precipitation of a microcrystalline solid. This solid was recrystallized in methanol giving dark red (almost black) needles of complex **2** suitable for single crystal X-ray analysis. Yield ca. 50%. Elemental analysis calcd (%) for C₃₂H₂₃Br₂F₆FeN₁₂O_{8.5}S₂: C, 34.77; H, 2.10; N, 15.21. Found: C, 34.63; H, 2.15; N, 15.41. μ=0 B.M.,

Synthesis of [Fe(L_{N4}=bptp)₂](BPh₄)₂·3CH₂Cl₂ (1): Under an argon atmosphere, a methanolic solution (15 mL) of Fe(BF₄)₂·6H₂O (27 mg, 0.08 mmol) was added drop-wise under stirring to a solution of the ligand L_{N3}=ptpp (56 mg, 0.16 mmol) in CH₂Cl₂ (20 mL). To the resulting red-violet solution a methanolic solution (10 mL) containing an excess of Na[B(C₆H₅)₄] (82 mg, 0.24 mmol) was added. Slow evaporation of this solution afforded dark-red needles and small red rhombohedral single crystals, which were separated mechanically. The former crystals were not suitable for single crystal analysis due to rapid deterioration, most likely due to the loss of included solvent. As complex **2**, this product resulted to be diamagnetic suggesting that the needles consisted of [Fe(L_{N3}=ptpp)₂](BPh₄)₂ species. The rhombohedral red sample was appropriate for single crystal analysis and corresponds to complex **1**. Yield ca. 10%. Elemental analysis calcd (%) for C₉₅H₇₄B₂Cl₆FeN₁₆: C, 65.96; H, 4.31; N, 12.96. Found: 64.81; H, 4.39; N, 12.70. μ=5.29 B.M.

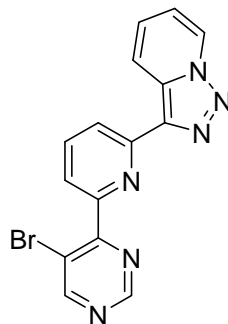
Single crystal X-ray diffraction: Single-crystal X-ray data of **1** and **2** were collected at 120 K with a SuperNova Sapphire3 single crystal diffractometer using Mo K_α (λ = 0.71073 Å). A data scaling and empirical absorption correction was performed. The structures were solved by direct methods using SHELXS-2014 and refined by full-matrix least squares on *F*² using SHELXL-2014.^[16] All non-hydrogen atoms were refined anisotropically, except for C32 and C32A (compound **2**). Hydrogen atoms except for water molecules in compound **2** were placed in calculated positions refined by using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. CCDC-1439487 (**1**), CCDC-1439488 (**2**).

Magnetic measurements: Variable-temperature magnetic susceptibility measurements were recorded for single crystals and microcrystalline samples of **1** and **2** at a scanning rate of 2 K/min with a Quantum Design MPMS2 SQUID susceptometer equipped with a 7 T magnet, operating at 1 T and at temperatures 5–400 K. Experimental susceptibilities were corrected from diamagnetism of the constituent atoms by the use of Pascal's constants.

General procedures

Starting materials, if commercially available, were purchased and used as such, provided that suitable checks (melting ranges, refractive indices and gas chromatography) had confirmed the claimed purity. When known compounds had to be prepared by literature procedures, pertinent references are given. Air- and moisture-sensitive materials were stored in Schlenk tubes. They were protected by and handled under argon, in appropriate glassware. Tetrahydrofuran was dried by distillation from sodium after the characteristic blue colour of sodium diphenyl ketyl. Melting points or ranges (m.p.) given were determined on a Kofler heated stage and found to be reproducible after recrystallization, unless stated otherwise (“decomp.”). Column chromatography was carried out on a column packed with silica gel (60N spherical neutral size 63–210 μm). ^1H and (^1H decoupled) ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at 400 or 300 and 101 or 75 MHz, respectively. Chemical shifts are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform ($\delta = 7.27$ ppm). Coupling constants (J) are given in Hz. Coupling patterns are abbreviated as, for example, s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sp (septuplet), td (triplet of doublets), m (multiplet), app. s (apparent singlet) and br. (broad). COSY experiments were performed for all compounds. HRMS Electron Impact (EI) or ElectroSpray (ES) determinations were made using a VG Autospec Trio 1000 (Fisons). The solvents used were of spectroscopic or equivalent grade. Water was twice distilled and passed through a Millipore apparatus. UV-Vis absorption spectra were recorded on an Agilent 8453 spectroscopy system. The emission spectra were recorded with a PTI MO-5020 spectrofluorimeter in the 300–500 nm range.

3-(6-(5-bromopyrimidin-4-yl)pyridin-2-yl)-[1,2,3]triazolo[1,5-a] pyridine = L_{N3} = ptp
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May05-2009
ab9220
proton CDCl3 u ABAR 4

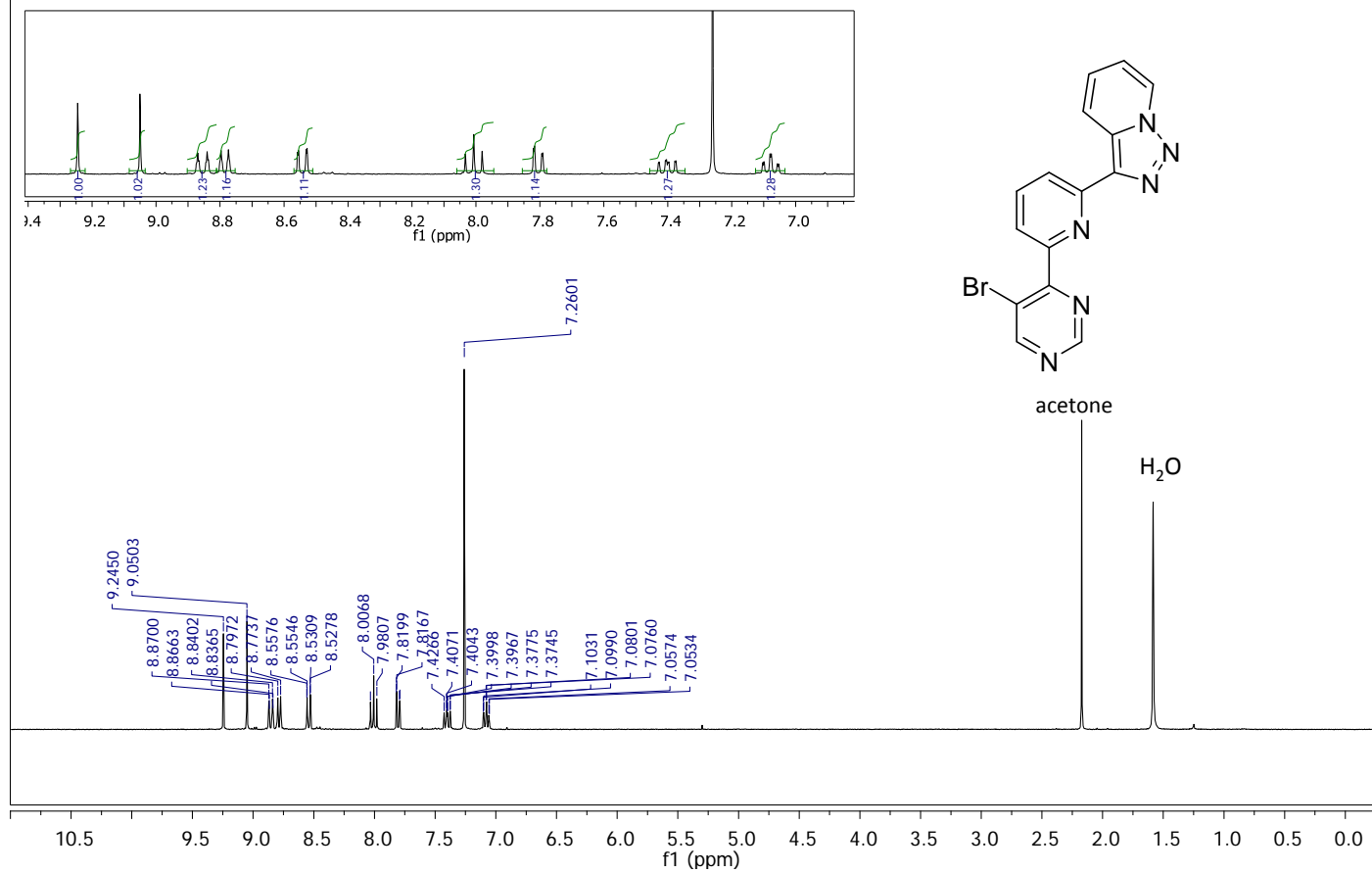


Figure S1: ¹H NMR (300 MHz, CDCl₃) of ptp

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c13cpdc CDCl3 u ABAR 10

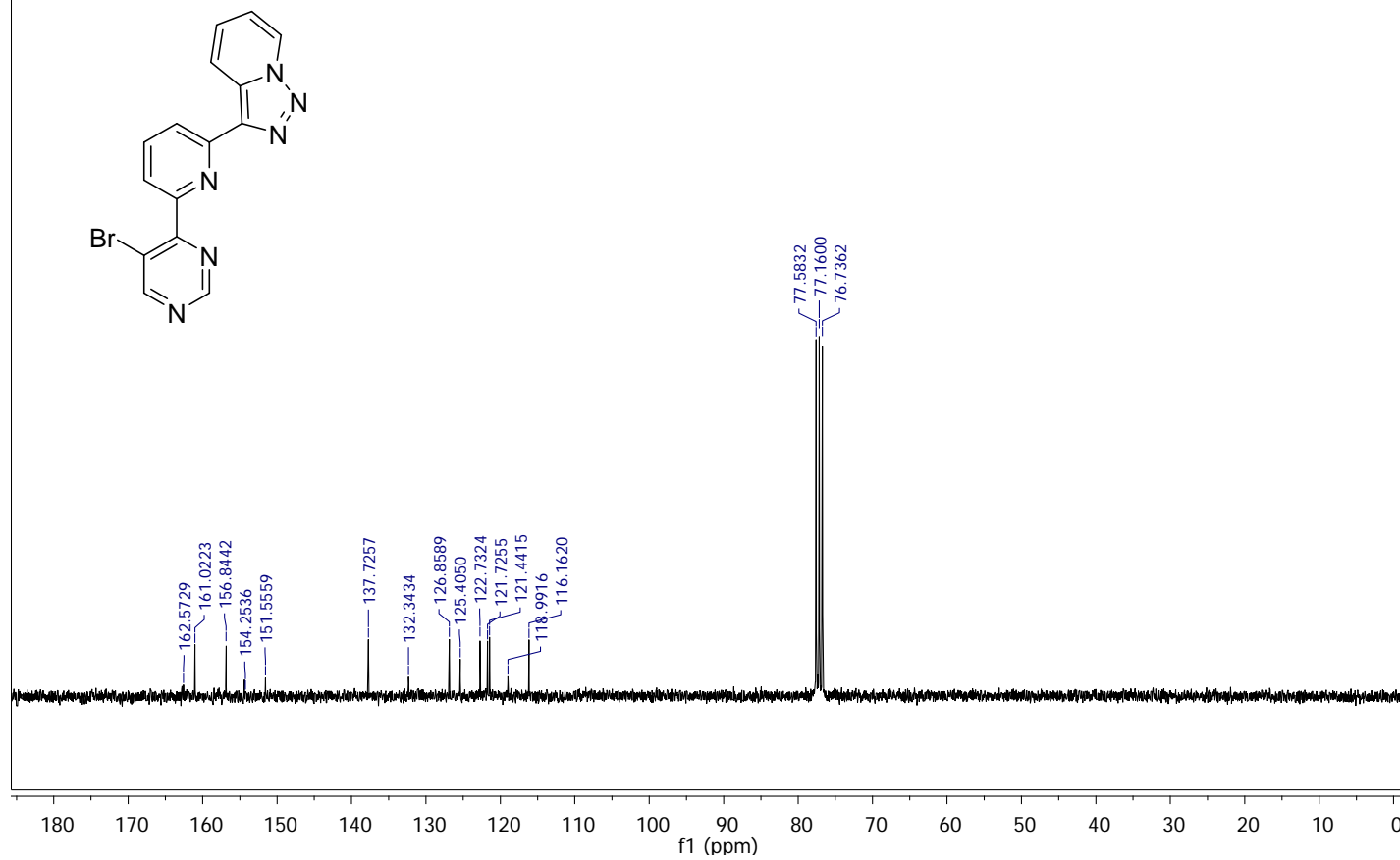
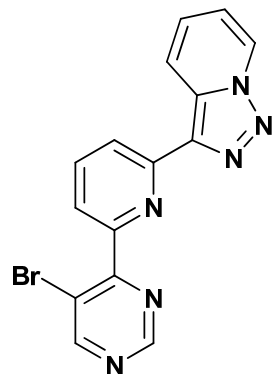


Figure S2: ¹³C NMR (75.5 MHz, CDCl₃) of ptp



[Fe(II)]	0.000199	M
[Ligand]	0.00005662	M

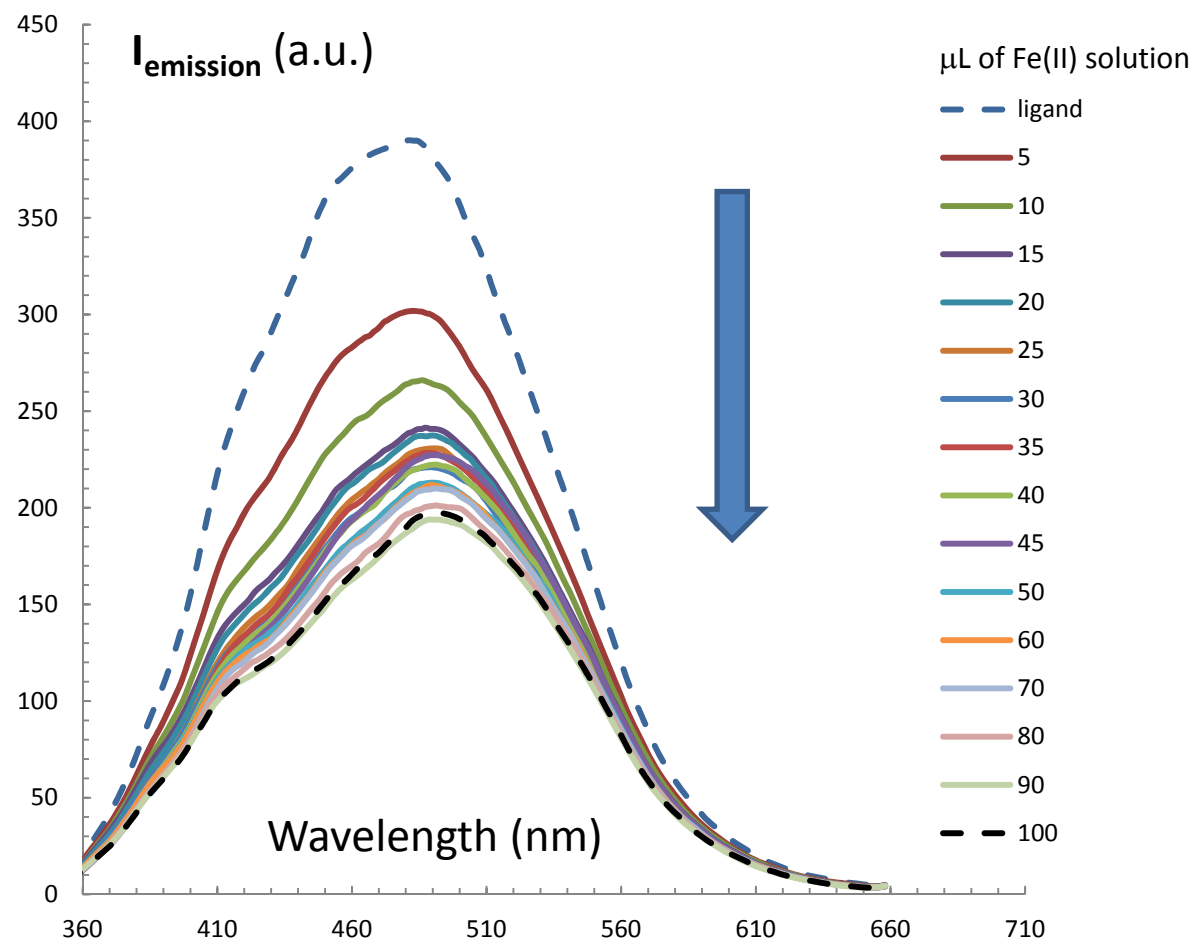


Figure S3: Fluorescence Quenching of **7B** upon addition of Fe(II) sulphate salt (volume in μL).
(Note: a.u.=arbitrary units)

V	2.05	mL
[ligand]	0.000069049	M
[FeII]	0.000199	M

V add (μL)	Int	Int Norm	[Fe(II)]
0	389.986857	1	0
5	301.437143	0.7729418	4.8418E-07
10	264.081	0.67715359	9.6602E-07
15	238.195286	0.61077773	1.4455E-06
20	234.276571	0.6007294	1.9227E-06
25	227.188714	0.5825548	2.3976E-06
30	217.978286	0.55893752	2.8702E-06
35	224.493714	0.57564431	3.3405E-06
40	218.045571	0.55911005	3.8086E-06
45	221.610286	0.56825065	4.2745E-06
50	208.594143	0.5348748	4.7381E-06
60	205.777286	0.52765185	5.6588E-06
70	204.842143	0.52525396	6.5708E-06
80	196.777143	0.50457378	7.4742E-06
90	187.771	0.48148033	8.3692E-06
100	191.094571	0.49000259	9.2558E-06

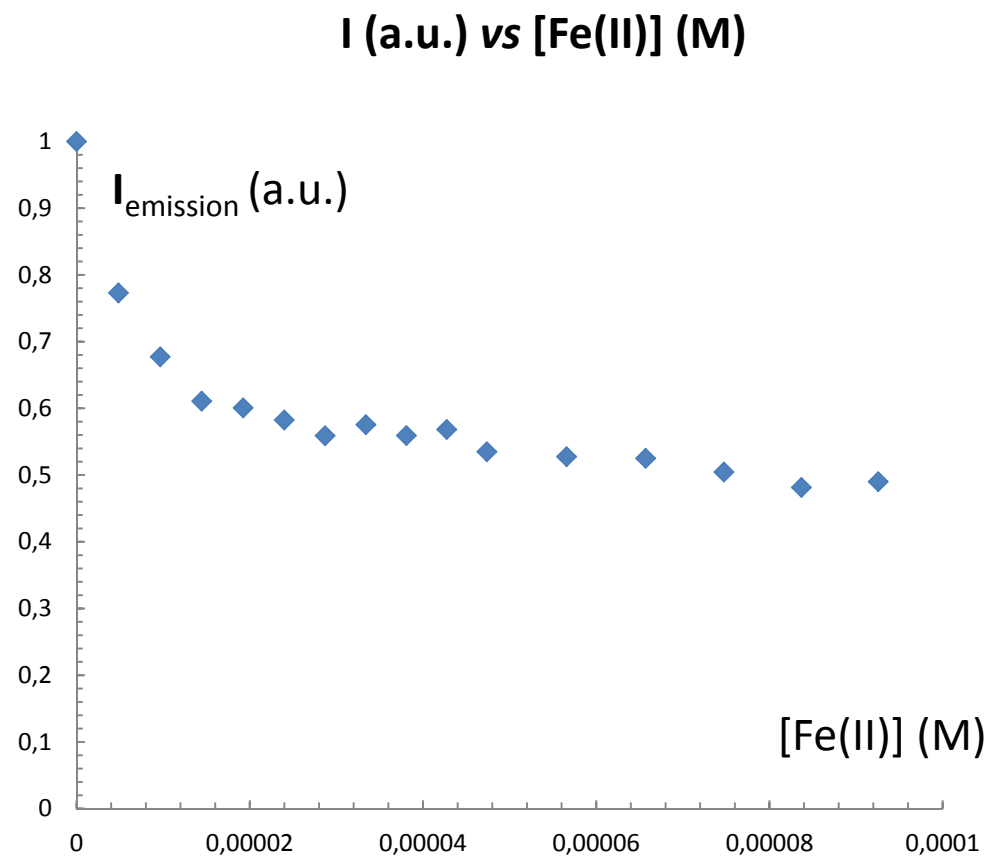
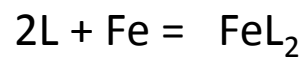


Figure S4: Fluorescence Quenching of **ptpp** upon addition of Fe(II) sulphate salt (volume in μL) at 482 nm.

(Note: a.u.=arbitrary units)



$$\text{Stern-Volmer eq: } I_0/I = 1 + K_{SV} * [Fe(II)]^{0.5}$$

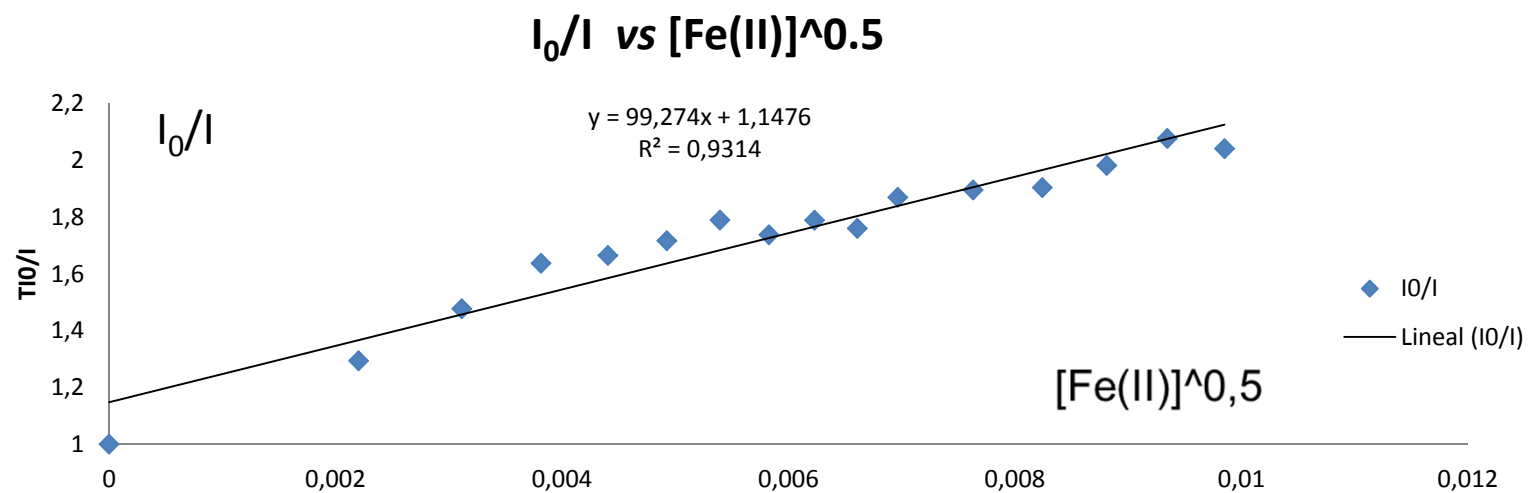


Figure S5: Stern-Volmer plot of **ptpp** upon addition of Fe(II) sulphate salt at 482 nm.

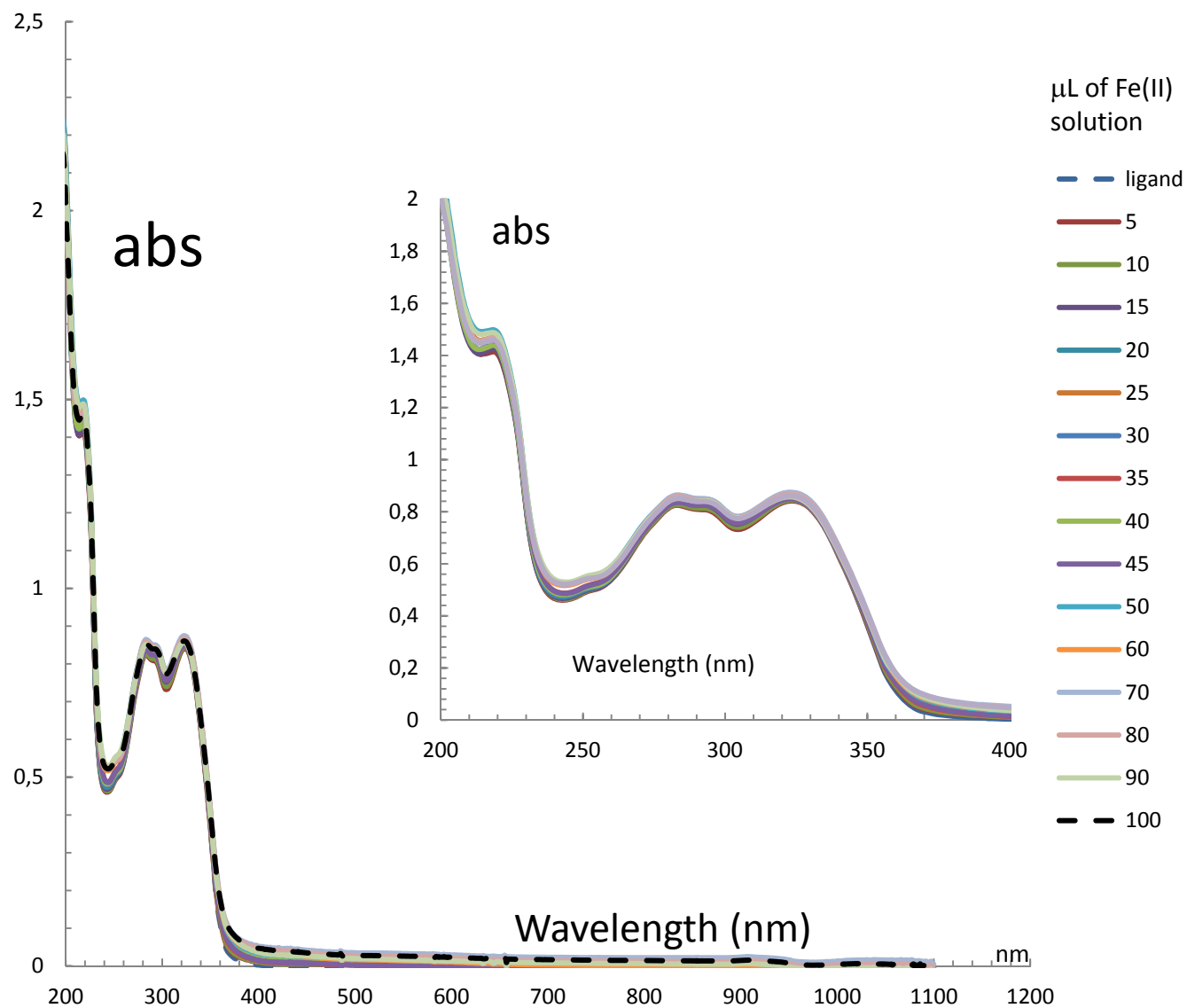
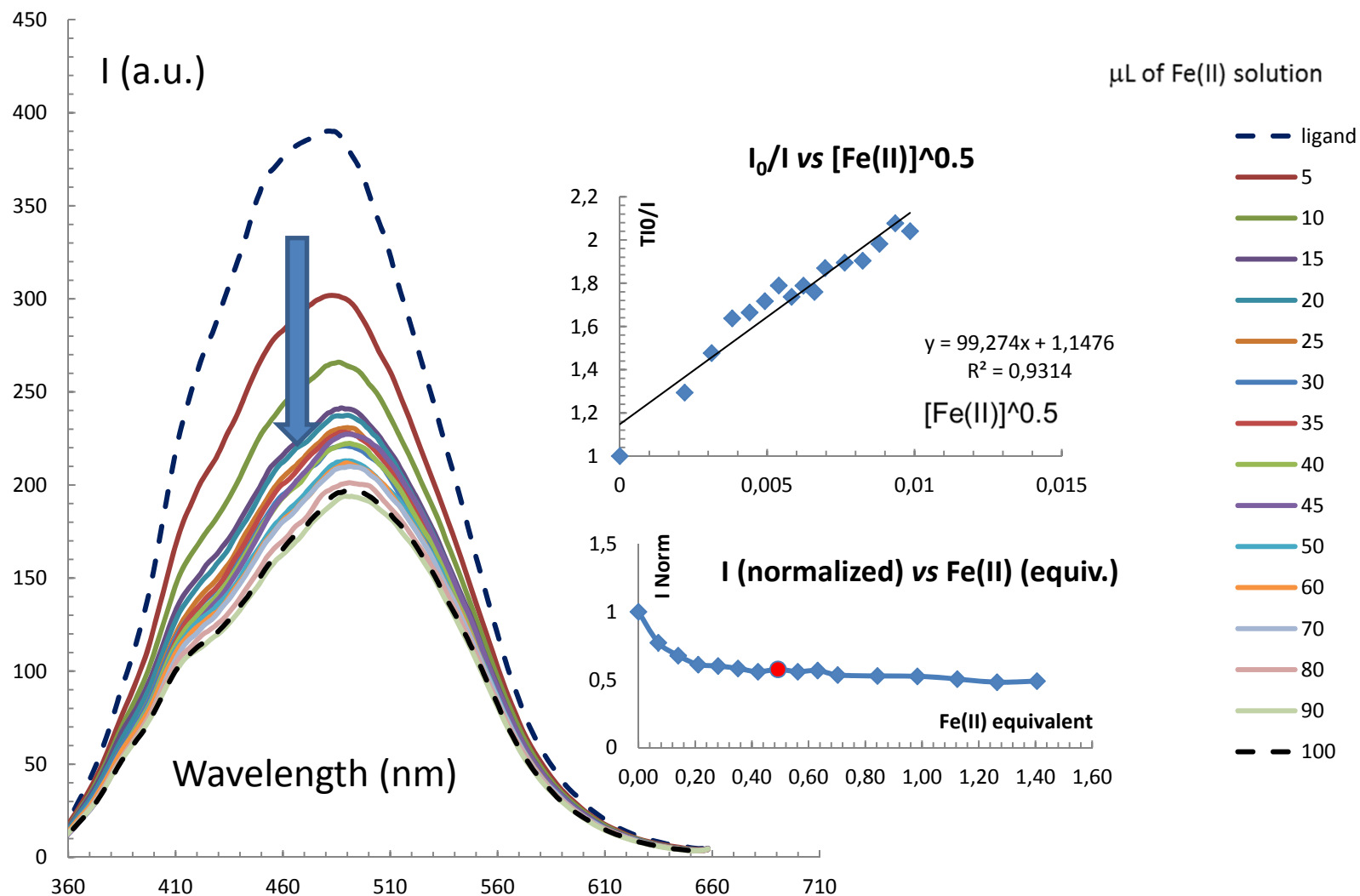


Figure S6: UV/Vis of **ptpp** upon addition of Fe(II) sulphate salt (volume in μL).
Inset: 200-400 nm domain

CONCLUSION

UV/Vis titration of compound **ptpp** with Fe(II) Sulfate did not afford any significant modification of the spectra, however fluorescence emission was quenched in this experience (Figure YY) without either hypsochromic or bathochromic displacement. Stern-Volmer analysis adjusted to the stoichiometry of 2 ligands and one iron (II) atom allowed the obtention of a quenching constant ($K = 99.72$). The quenching can be explained by the formation of low spin complex that absorbs the emission of the ligand. Furthermore, significant variations of the emission are only observed before reaching 2(L) to 1 (FeII) stoichiometry being in agreement with such kind of complex.



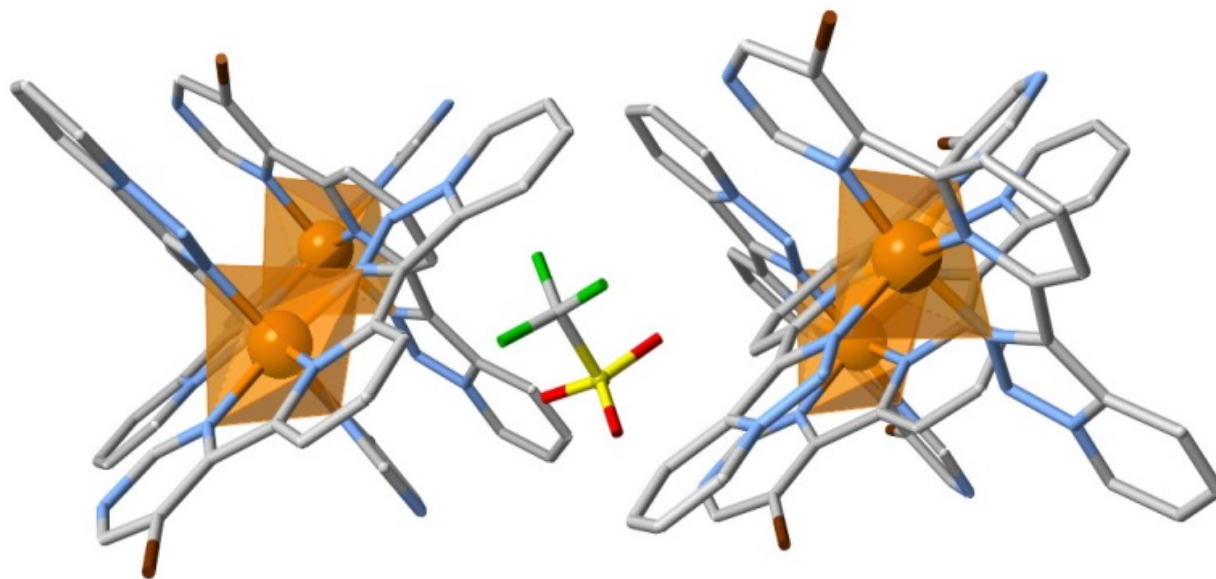
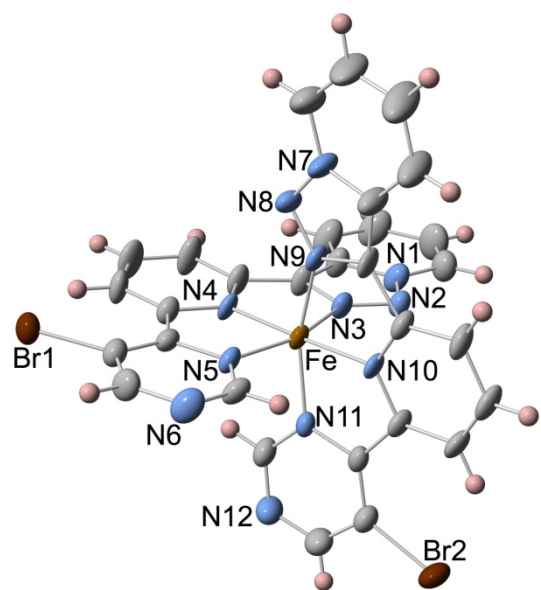


Figure S7: ORTEP representation of the cation $[\text{Fe}(\text{L}_{\text{N}_3}=\text{ptpp})_2]^{2+}$

Thermal ellipsoids at 40% probability level. Color code: C, grey; N, blue; H, pink; Br, red; Fe, orange.

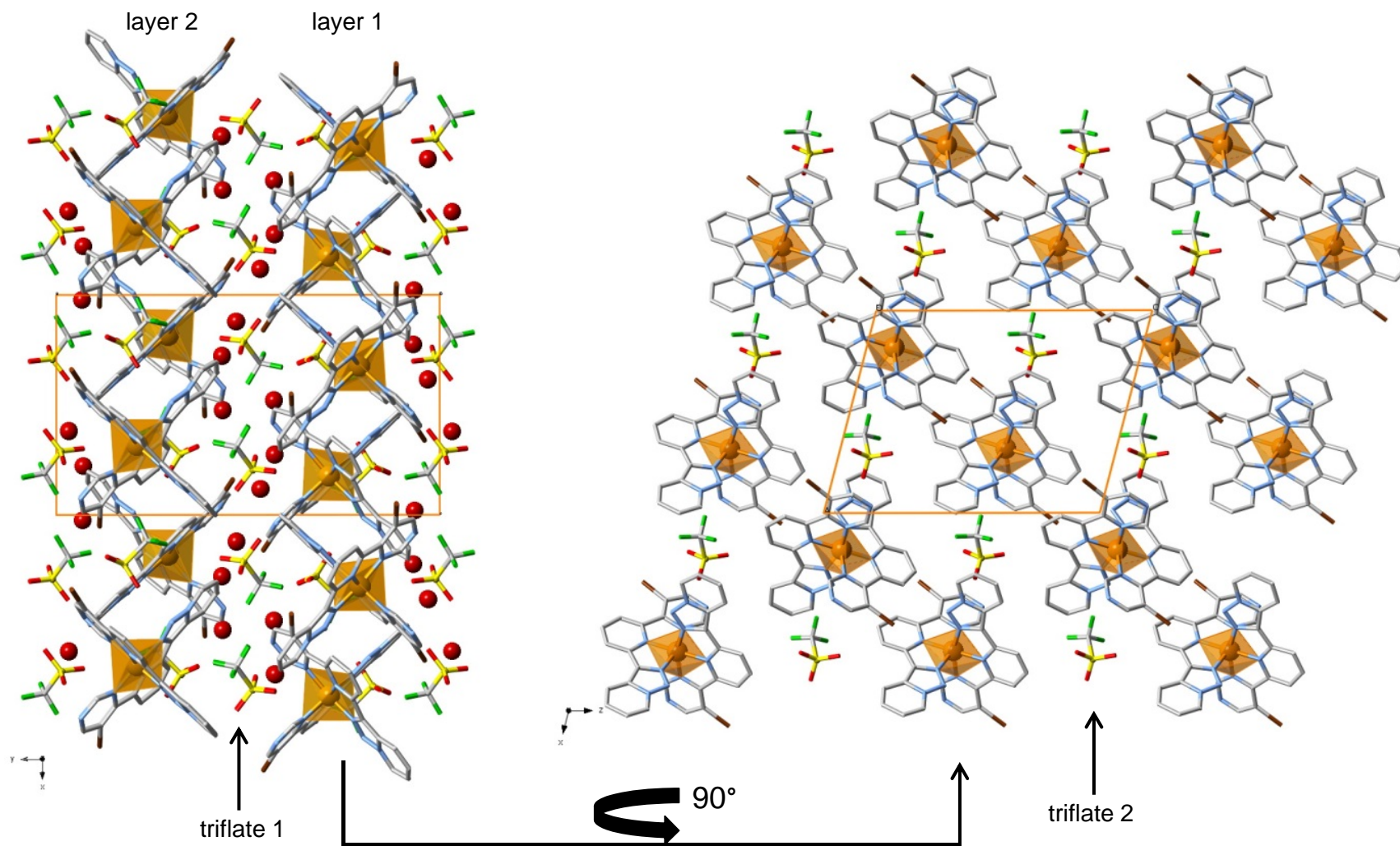


Figure S8: Packing of $[\text{Fe}(\text{L}_{\text{N}3}=\text{ptpp})_2]^{2+}$

Color code: C, grey; N, blue; H, pink; Br, red; Fe, orange.

Table S1. Crystal data of compound **1** and **2**

	1 (120 K)	2 (120 K)
Empirical formula	C ₉₅ H ₇₄ N ₁₆ Cl ₆ B ₂ Fe	C ₃₂ H ₂₃ O _{8.5} N ₁₂ S ₂ F ₆ Br ₂ Fe
Mr	1729.87	1105.41
Crystal system	triclinic	monoclinic
Space group	P-1	P 2 ₁ /c
<i>a</i> (Å)	14.0950(5)	12.3280(6)
<i>b</i> (Å)	15.6670(5)	20.6970(8)
<i>c</i> (Å)	21.1820(8)	17.7258(10)
α (°)	86.503(3)	
β (°)	76.211(3)	117.720(4)
γ (°)	69.422(3)	
<i>V</i> (Å ³)	4251.6(3)	4003.7(3)
<i>Z</i>	2	4
<i>D</i> _c (mg cm ⁻³)	1.351	1.834
<i>F</i> (000)	1788	2196
μ (Mo-K _α)(mm ⁻¹)	0.424	2.573
Crystal size (mm)	0.04x0.04x0.10	0.10 x 0.15 x 0.15
Temperature (K)	120(1)	120(1)
No. of total reflections	21688	11180
No. of reflections [<i>I</i> >2σ(<i>I</i>)]	12389	5794
<i>R</i> [<i>I</i> >2σ(<i>I</i>)]	0.0909	0.0885
<i>R</i> [all data]	0.1551	0.1584
<i>S</i>	1.022	0.952

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.
 $w = 1 / [\sigma^2(F_o^2) + (m P)^2 + n P]$ where $P = (F_o^2 + 2F_c^2) / 3$;
 $m = 0.2000$ (**1**) and 0.1826 (**2**); $n = 0.0000$ (**1**) and 16.4468 (**2**)

Table S2. Selected bond lengths [\AA] and angles [$^\circ$] for **1** and **2**

	1 (120 K)	2 (120 K)
Fe-N(3)	2.292(3)	1.951(6)
Fe-N(4)	2.328(3)	1.903(5)
Fe-N(5)	2.321(3)	1.958(6)
Fe-N(9)		1.941(6)
Fe-N(10)		1.907(5)
Fe-N(11)		1.960(6)
Fe-N(6)	2.267(3)	
Fe-N(11)	2.279(3)	
Fe-N(12)	2.363(3)	
Fe-N(13)	2.339(3)	
Fe-N(14)	2.318(3)	
N(3)-Fe-N(4)	69.63(11)	81.6(2)
N(3)-Fe-N(5)	137.80(12)	161.5(2)
N(3)-Fe-N(9)		92.2(3)
N(3)-Fe-N(10)		97.8(2)
N(3)-Fe-N(11)		91.3(2)
N(4)-Fe-N(5)		80.0(2)
N(4)-Fe-N(9)		96.8(2)
N(4)-Fe-N(10)		178.1(3)
N(4)-Fe-N(11)		102.2(2)
N(5)-Fe-N(9)		90.1(3)
N(5)-Fe-N(10)		100.6(2)
N(5)-Fe-N(11)		92.5(2)
N(9)-Fe-N(10)		81.5(2)
N(9)-Fe-N(11)		161.1(2)
N(10)-Fe-N(11)		79.6(2)
N(3)-Fe-N(6)	152.35(12)	
N(3)-Fe-N(11)	93.46(12)	
N(3)-Fe-N(12)	78.41(11)	
N(3)-Fe-N(13)	75.99(12)	
N(3)-Fe-N(14)	96.76(12)	
N(4)-Fe-N(5)	68.28(11)	
N(4)-Fe-N(6)	138.01(11)	
N(4)-Fe-N(11)	81.62(12)	
N(4)-Fe-N(12)	134.79(11)	
N(4)-Fe-N(13)	130.29(11)	
N(4)-Fe-N(14)	80.18(11)	
N(5)-Fe-N(6)	69.76(11)	
N(5)-Fe-N(11)	77.74(11)	
N(5)-Fe-N(12)	132.54(11)	
N(5)-Fe-N(13)	136.90(11)	
N(5)-Fe-N(14)	79.02(11)	
N(6)-Fe-N(11)	91.02(12)	
N(6)-Fe-N(12)	77.79(11)	
N(6)-Fe-N(13)	81.91(11)	
N(6)-Fe-N(14)	90.67(11)	
N(11)-Fe-N(12)	69.02(12)	

Table S3: Selected intermolecular interactions measured from X-ray for **1**

C---C triazol- Ph₄B⁻

C(1)---C(91) = 3.575(13) (1-2)
C(2)---C(58)' = 3.547(11) (1-1) (-x+2, -y+1, -z+1)
C(3)---C(46)' = 3.599(11) (1-1) (-x+2, -y+1, -z+1)
C(3)---C(47)' = 3.575(12) (1-1) (-x+2, -y+1, -z+1)
C(3)---C(48)' = 3.573(13) (1-1) (-x+2, -y+1, -z+1)
C(3)---C(49)' = 3.576(14) (1-1) (-x+2, -y+1, -z+1)
C(17)---C(85)' = 3.323(9) (2-2) (x, y-1, z)
C(18)---C(84)' = 3.253(9) (2-2) (x, y-1, z)
C(18)---C(85)' = 3.331(8) (2-2) (x, y-1, z)
C(19)---C(74)' = 3.574(9) (2-2) (x, y-1, z)
C(19)---C(83)' = 3.492(9) (2-2) (x, y-1, z)
C(19)---C(84)' = 3.452(8) (2-2) (x, y-1, z)
C(19)---C(85)' = 3.582(8) (2-2) (x, y-1, z)
C(20)---C(83)' = 3.458(9) (2-2) (x, y-1, z)
C(23)---C(60)' = 3.338(11) (3-1) (-x+2, -y, -z+1)
C(24)---C(63)' = 3.596(9) (3-1) (x-1, y, z)
C(24)---C(68)' = 3.574(10) (3-1) (x-1, y, z)
C(25)---C(46)' = 3.585(10) (3-1) (x-1, y, z)
C(25)---C(68)' = 3.522(10) (3-1) (x-1, y, z)
C(42)---C(83)' = 3.495(8) (4-2) (x+1, y-1, z)
C(42)---C(84)' = 3.392(9) (4-2) (x+1, y-1, z)

C-C bipy- Ph₄B⁻

C(9)---C(64)' = 3.566(11) (1-1) (-x+2, -y, -z+1)
C(9)---C(65)' = 3.419(11) (1-1) (-x+2, -y, -z+1)
C(10)---C(52)' = 3.588(9) (1-1) (-x+2, -y, -z+1)
C(14)---C(71)' = 3.542(11) (1-2) (x, y-1, z)
C(16)---C(85)' = 3.559(10) (1-2) (x, y-1, z)
C(35)---C(76) = 3.545(9) (2-2)
C(36)---C(71) = 3.589(11) (2-2)
C(37)---C(76)' = 3.552(9) (1-2) (-x+2, -y+1, -z)

C---C benzotriazol-bipy

C(5)---C(15)' = 3.377(8) (1-1) (-x+2, -y+1, -z+1)
C(16)---C(21)' = 3.475(8) (2-1) (-x+2, -y, -z)

C---C benzotriazol-benzotriazol

C(17)---C(20)' = 3.349(8) (2-2) (-x+2, -y, -z)
C(17)---C(21)' = 3.401(8) (2-2) (-x+2, -y, -z)
C(18)---C(18)' = 3.516(7) (2-2) (-x+2, -y, -z)
C(18)---C(19)' = 3.415(8) (2-2) (-x+2, -y, -z)
C(18)---C(20)' = 3.467(9) (2-2) (-x+2, -y, -z)
C(25)---C(43)' = 3.490(12) (3-4) (x-1, y, z)
C(26)---C(42)' = 3.582(12) (3-4) (x-1, y, z)
C(48)---C(55)' = 3.572(10) (1-1) (-x+2, -y+1, -z+1)

C---C Ph₄B⁻-dichloromethane

C(48)---C(95)' = 3.40 (2) (1-3) (-x+2, -y+1, -z+1)
C(49)---C(95)' = 3.48(2) (1-3) (-x+2, -y+1, -z+1)

Cl---C y Cl---N

Cl(2)---C(21)' = 3.625(7) (triazol2) (-x+1, -y+1, -z)
Cl(5)---N(1)' = 3.209(7) (triazol1) (-x+2, -y+1, -z+1)
Cl(5)---C(5)' = 3.377(8) (triazol1) (-x+2, -y+1, -z+1)
Cl(5)---C(49)' = 3.638(10) (Ph₄B⁻1) (-x+2, -y+1, -z+1)

Table S4: Selected intermolecular interactions measured from X-ray for **2**

benzotriazole- triflate

C(1)---O(3) = 3.310(10) (1-1)
C(3)---O(1) = 3.37(2) (1-1) (-x-1, -y-1, -z-1)
C(4)---O(5) = 3.231(14) (1-2) (x, -y-1/2, z-1/2)
C(16)---O(1) = 3.29(2) (2-1) (-x, -y-1, -z-1)
N(1)---F(3) = 3.06(2) (1-1)
N(2)---F(2) = 3.07(2) (1-1)
N(9)---F(2) = 3.070(13) (2-1)
C(1)---F(3) = 3.18(2) (1-1)
C(1)---F(4) = 3.05(2) (1-2)
C(20)---F(2) = 3.03(2) (2-1)
C(21)---F(2) = 2.960(13) (2-1)

benzotriazole-water

C(1)---O(8) = 3.43(2) (1-2)
C(3)---O(8) = 3.53(2) (1-2) (-x-1, -y-1, -z-1)
C(18)---O(8) = 3.20(2) (2-2) (x+1, y, z)
C(18)---O(9) = 3.54(2) (2-3) (x+1, -y-1/2, z+1/2)
C(19)---O(7) = 3.298(14) (2-1) (x+1, -y-1/2, z+1/2)

pyridine-pyrimidine

C(10)---Br(1) = 3.264(9) (1-1)
N(10)---C(15) = 3.197(11) (2-1)
C(25)---Br(2) = 3.292(9) (2-2)
N(4)---C(30) = 3.241(12) (1-2)

pyrimidine-water

C(14)---O(9) = 3.18(2) (1-3) (-x, -y, -z-1)
C(30)---O(9A) = 3.08(2) (2-3)

pyridine-triflate

C(8)---O(5) = 3.672(12) (1-2) (x, -y-1/2, z-1/2)
C(10)---O(3) = 3.540(12) (2-2) (x, -y-1/2, z-1/2)
C(24)---O(4) = 3.596(10) (2-2) (x+1, -y-1/2, z+1/2)

pyrimidine-triflate

C(14)---O(6) = 3.07(2) (1-2) (x+1, y, z)
C(15)---O(1) = 3.465(12) (1-1) (-x, y+1/2, -z-1/2)
C(30)---F(6) = 3.151(12) (2-2)

pyridine-benzotriazole

N(8)---C(24) = 3.342(12) (2-2) (x, -y-1/2, z-1/2)

triflate-water

O(3)---O(8) = 2.79(2) (1-2)
O(6)---O(7) = 2.79(2) (2-1)

water-water

O(7)---O(9) = 2.73(3) (1-3)
O(8)---O(9A) = 3.04(2) (2-3) (x, -y-1/2, z+1/2)

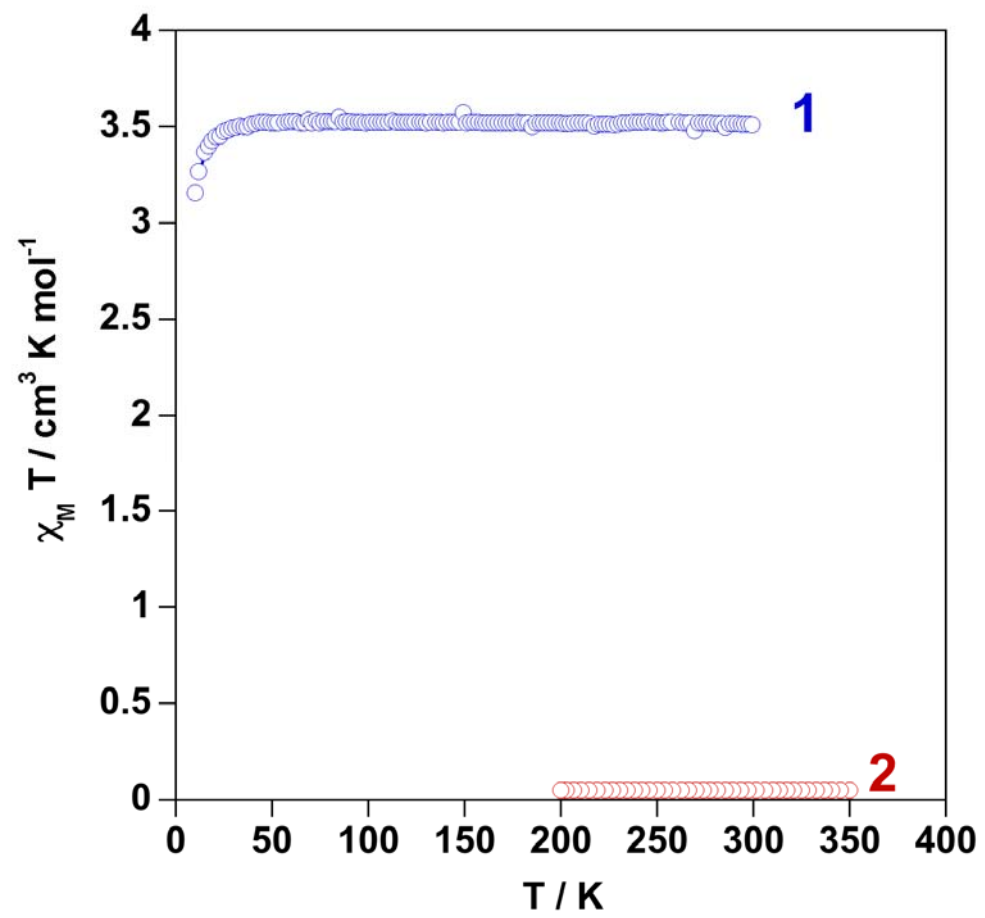


Figure S9: $\chi_M T$ vs T plot for complexes **1** and **2**