Iron complexes of bridging azo ligands in aqueous solution; changes in the thermal switching mechanism on coordination and oxidation state of metal centres

Manuel Bardají,[a] *Mercè Font-Bardia,*[b] *Albert Gallen,*[c] *Beltzane Garcia-Cirera,*[c] *Montserrat Ferrer,*[c,d*] *and Manuel Martínez*[c,d*]

[a] IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain

[b] Unitat de Difracció de RX, Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB). Universitat de Barcelona, Solé i Sabarís 1-3, 08028 Barcelona, Spain

[c] Secció de Química Inorgànica, Departament de Química Inorgànica i Orgànica. Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

[d] Institute of Nanoscience and Nanotechnology (IN2UB), Universitat de Barcelona, 08028 Barcelona, Spain

montse.ferrer@qi.ub.edu, manel.martinez@qi.ub.edu

SUPPORTING INFORMATION

Synthesis and characterization of the ligands

According to the literature,[1-2] the synthesis of the isocyanide azo derivatives has been carried out in three steps that are outlined as follows:

Synthesis of 4-((4-isocyanophenyl)diazenyl)pyridine, $CN(C_6H_4)$-N=N-(C_5H_4N)

Step 1: **4-((4-aminophenyl)diazenyl)pyridine.** 4-aminopyridine (3 g, 32 mmol) was suspended in tetrafluoroboric acid (23 cm^3, 50 % in water). The resulting suspension was cooled down to 0 ºC with an ice bath. The formation of a white milky solution is observed. Then, sodium nitrite (2.2 g, 32 mmol) was added slowly keeping the temperature at 0 ºC and the color of the resulting solution becomes pale yellow. After stirring at 0 ºC for further 30 minutes, aniline (6 g, 64 mmol) was added and the formation of a dark brown suspension was observed. The reaction mixture was stirred at room temperature for 30 minutes. The addition of a concentrated NaOH solution (22 g NaOH in 75 mL water) led to the precipitation of a dark brown solid that was filtered and washed thoroughly with water and acetonitrile to obtain the product as an orange solid (1.37 g, 22%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.73 (d,[3] J_{HH} = 6.2 Hz, 2H, $H_{\alpha\text{-py}}$), 7.84 (d, J_{HH} = 7.7 Hz, 2H, H_{meta} $PhNH_2$), 7.63 (d, J_{HH} = 6.2 Hz, 2H, $H_{\beta\text{-py}}$), 6.75 (d, J_{HH} = 7.7 Hz, 2H, $H_{ortho}PhNH_2$), 4.22 (s, 2H, NH_2).

Step 2: **N-(4-(pyridin-4-yldiazenyl)phenyl)formamide.** In a N_2 purged Schlenk flask 1 mL (26 mmol) of formic acid and 2.5 mL (26 mmol) of acetic anhydride were added and stirred for 2 h at 50-60 °C. After cooling to room temperature 4-((4-aminophenyl)diazenyl)pyridine (2.20 g, 11 mmol) and 75-100 mL of dry Et_2O were subsequently added. After 60 h of stirring the desired product was obtained as an orange solid that was filtered and vacuum dried. (2.42 g, 96%). ^{1}H NMR (DMSO-d_6 , 400 MHz): δ (*cis ca.* 80%) 10.67 (s, 1H, NH), 8.81 (d, J_{HH} = 5.2 Hz, $H_{\alpha\text{-py}}$), 8.39 (s, 1H, -CO-H), 7.97 (d, J_{HH} = 8.5 Hz, $H_{meta}PhNH$), 7.85 (d, J_{HH} = 8.5 Hz, 2H, $H_{ortho}PhNH$), 7.72 (d, J_{HH} = 5.2 Hz, $H_{\beta\text{-py}}$); (*trans ca.* 20%) 10.58 (d, J_{HH} = 10.1 Hz, 1H, NH), 9.04 (d, J_{HH} = 10.3 Hz, 1H, -CO-H), 8.81 (superimposed with the isomer *cis* signal, 2H, $H_{\alpha\text{-py}}$), 7.97 (superimposed with the isomer *cis* signal, $H_{meta}PhNH$), 7.72 (superimposed with the isomer *cis* signal, $H_{\beta\text{-py}}$), 7.45 (d, J_{HH} = 8.4 Hz, 2H, $H_{ortho}PhNH$).

Step 3: **4-((4-isocyanophenyl)diazenyl)pyridine.** N-(4-(pyridin-4-yldiazenyl)phenyl)formamide (2.5 g, 11 mmol) was dissolved in 50 mL of dry CH_2Cl_2 under N_2 atmosphere. After adding triethylamine (3 mL, 21 mmol) the mixture was cooled down to 0 ºC and a solution of triphosgene (1.1 g, 3.7 mmol) in 20 mL of dry CH_2Cl_2 was added dropwise. The reaction mixture was left under stirring overnight at room temperature and a brown suspension was obtained that was treated with a saturated aqueous Na_2CO_3 solution. After extracting three times with CH_2Cl_2 the combined organic layers were dried over Na_2SO_4 and the dark red solution obtained taken to dryness. The crude product was dissolved in the minimum volume of CH_2Cl_2 and purified by column chromatography on silica gel using CH_2Cl_2:CH_3OH 100:1 to get 1.1 g of an orange solid. Yield: 48%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (*trans*) 8.84 (d, J_{HH} = 6.2 Hz, 2H, $H_{\alpha\text{-py}}$), 8.01 (d, J_{HH} = 8.4 Hz, 2H, $H_{meta}PhNC$), 7.72 (d, J_{HH} = 6.1 Hz, 2H, $H_{\beta\text{-py}}$), 7.56 (d, J_{HH} = 8.6 Hz, 2H, $H_{ortho}PhNC$). ^{1}H NMR (CD_3OD, 400 MHz): δ (*trans*) 8.79 (d, J_{HH} = 6.2 Hz, 2H, $H_{\alpha\text{-py}}$), 8.09 (d, J_{HH} =

8.5 Hz, 2H, H_{meta}PhNC), 7.86 (d, J_{HH} = 6.3 Hz, 2H, $H_{\beta\text{-py}}$), 7.71 (d, J_{HH} = 8.5. Hz, 2H, H_{ortho}PhNC); (*cis* after irradiation) 8.46 (d, J_{HH} = 6.3 Hz, 2H, $H_{\alpha\text{-py}}$), 8.42 (d, J_{HH} = 8.6 Hz, 2H, H_{meta}PhNC), 6.99 (d, J_{HH} = 8.6 Hz, 2H, H_{ortho}PhNC), 6.88 (d, J_{HH} = 6.3 Hz, 2H, $H_{\beta\text{-py}}$). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (*trans*) 167.2 (NC), 156.7($C_{q\text{-N=N}}$), 151.7 ($C_{q\text{-N=N}}$), 151.7 ($C_{\alpha\text{-py}}$), 129.4 (br, C_q-NC), 127.6 (C_{ortho}PhNC), 124.6 (C_{meta}PhNC) , 116.4 ($C_{\beta\text{-py}}$). IR ($\nu_{(CN)}$): 2142 cm^{-1}. MS (ESI+) m/z: {[CN(C_6H_4)-N=N-(C_5H_4N)]+H^+}$^+$, 209.08 (*calc.* 209.08). UV-vis (Toluene) [λ_{max}, nm (ε, M^{-1} cm^{-1})] (toluene) 318 (22800), 465 (420); (methanol) 314 (22700), 440 (760). CV (Acetonitrile, *vs* NHE, ferrocene reference): -619, -1070 mV.

Synthesis of 4-((4-isocyanophenyl)diazenyl)benzonitrile, CN(C_6H_4)-N=N-(C_5H_4)CN

Step 1: **4-((4-aminophenyl)diazenyl)benzonitrile.** This compound was prepared following the same procedure as described above for the compound 4-((4-aminophenyl)diazenyl)pyridine. From 4-aminobenzonitrile (3.8 g, 32 mmol), 1.1 g of the desired compound were obtained (15% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (d, J_{HH} = 8.8 Hz, 2H, H_{meta}PhCN), 7.84 (d, J_{HH} = 8.8 Hz, 2H, H_{meta}PhNH$_2$), 7.76 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H_{ortho}PhCN), 6.75 (d, $^3J_{HH}$ = 8.8 Hz, 2H, H_{ortho}PhNH$_2$), 4.22 (s, 2H, NH$_2$).

Step 2: **N-(4-(cyanophenyl)diazenyl)phenyl)formamide.** In a N_2 purged Schlenk flask 2.5 mL (66 mmol) of formic acid and 6.2 mL (66 mmol) of acetic anhydride were added and stirred for 2 h at 50-60 °C. After cooling to room temperature 4-((4-aminophenyl)diazenyl)benzonitrile (1.0 g, 4.5 mmol) and 75-100 mL of dry THF were subsequently added. After 60 h of stirring the resulting suspension is taken to dryness and the resulting orange solid was vacuum dried while heating at 30 ºC for 24h. (1.10 g, 97%). ^{1}H NMR (DMSO-d_6 , 500 MHz): δ (*cis ca.* 70%) 10.82 (s, 1H, NH), 8.38 (s, 1H, -CO-H), 8.05 (d, J_{HH} = 8.1Hz, H_{meta}PhCN), 7.99-7.94 (m, H_{ortho}PhCN + H_{meta}PhNH), 7.85 (d, J_{HH} = 8.5 Hz, 2H, H_{ortho}PhNH); (*trans ca.* 30%) 10.59 (br s, 1H, NH), 9.02 (d, J_{HH} = 8.4 Hz, 1H, -CO-H), 8.05 (superimposed with the isomer *cis* signal, H_{meta}PhCN), 7.99-7.94 (superimposed with the isomer *cis* signals, H_{ortho}PhCN + H_{meta}PhNH), 7.45 (d, J_{HH} = 8.2 Hz , 2H, H_{ortho}PhNH).

Step 3: **4-((4-isocyanophenyl)diazenyl)benzonitrile**. This compound was prepared following a very similar procedure to that described above for the compound 4-((4-isocyanophenyl)diazenyl)pyridine. From N-(4-(cyanophenyl)diazenyl)phenyl)formamide (2.8 g, 11 mmol) the crude product was purified by column chromatography on silica gel using CH_2Cl_2 to get, after recrystallization in the same solvent, 0.9 g of the desired compound as a pure orange solid. Yield: 35%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (*trans*) 8.02-7.98 (m, 4H, H_{meta}PhCN+ H_{meta}PhNC), 7.84 (d, J_{HH} = 8.5 Hz, 2H, H_{ortho}PhCN), 7.57 (d, J_{HH} = 8.7 Hz, 2H, H_{ortho}PhNC). ^{1}H NMR (CD_3OD, 400 MHz): δ (***trans***) 8.09-8.05 (m, 4H, H_{meta}PhCN+ H_{meta}PhNC), 7.96 (d, J_{HH} = 8.8 Hz, 2H, H_{ortho}PhCN), 7.69 (d, J_{HH} = 8.7 Hz, 2H, H_{ortho}PhNC); (***cis*** after irradiation) 7.41 + signal obscured by H_{ortho}PhNC of *trans* isomer (H_{meta}Ph), 7.01 (d, J_{HH} = 8.7 Hz, 2H, H_{ortho}PhCN), 6.96 (d, J_{HH} = 8.8 Hz, 2H, H_{ortho}PhNC). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ (*trans*) 167.2 (NC), 154.2($C_{q\text{-N=N}}$), 151.9 ($C_{q\text{-N=N}}$), 133.5 (C_{ortho}PhCN), 129.1 (br, C_q-NC), 127.7 (C_{ortho}PhNC), 124.5 (C_{meta}PhNC), 123.7 (C_{meta}PhCN), 118.4 (CN), 114.9 (C_q-CN). IR ($\nu_{(CN)}$): 2227, 2127 cm^{-1}. MS (ESI+) m/z: {[CN(C_6H_4)-N=N-(C_6H_4)CN]+H^+}$^+$, 233.08 (*calc.* 233.08). UV-vis [λ_{max}, nm (ε, M^{-1} cm^{-1})] (toluene) 333 (21800), 452

(580); (methanol) 326 (23600), 450 (370). CV (Acetonitrile, *vs* NHE, ferrocene reference): -619, -1070 mV.

Synthesis of 4,4'-diisocyanoazobenzene, CN(C_6H_4)-N=N-(C_5H_4)NC

Step 1: **4,4'-diaminoazobenzene.** This compound was prepared accordingly to the described procedure.[4]

Step 2: **4,4´-diformamidoazobenzene.** This compound was prepared following the same procedure as described above for the compound N-(4-(cyanophenyl)diazenyl)phenyl)formamide. From 4,4'-diaminoazobenzene (1.0 g, 4.7 mmol), formic acid (6 mL, 159 mmol) and acetic acid (15 mL, 159 mmol) 1.10 g of the desired compound were obtained (87% yield). ^{1}H NMR (DMSO-d_6, 400 MHz): δ (*cis-cis ca.* 80%) 10.53 (s, 2H, NH), 8.35 (s, 2H, -CO-H), 7.87 (m, 8.85 Hz, H_{meta}PhNH), 7.79 (d, J_{HH} = 8.9 Hz, 4H, H_{ortho}PhCN); (*trans-trans ca.* 20%) 10.46 (d, J_{HH} = 10.8 Hz, 2H, NH), 8.97 (d, J_{HH} = 10.8 Hz, 2H, -CO-H), 7.87 (superimposed with the isomer *cis-cis* signal, H_{meta}PhNH), 7.40 (d, J_{HH} = 8.5 Hz, 4H, H_{meta}PhNH).

Step 3: **4,4'-diisocyanoazobenzene**. This compound was prepared following a very similar procedure to that described above for the compound 4-((4-isocyanophenyl)diazenyl)pyridine. From 4,4´-diformamidoazobenzene (1.5 g, 5.6 mmol) the crude product was washed with CH_3OH and purified by column chromatography on silica gel using CH_2Cl_2 to get after concentration to vacuum of the eluate 0.6 g of the desired compound as a pure orange solid. Yield: 36%. ^{1}H NMR in $CDCl_3$ of both isomers of the compound agrees with the data available in the literature.[5] ^{1}H NMR (CD_3OD, 400 MHz): δ (*trans*) 8.04 (d, J_{HH} = 8.8 Hz, 2H, H_{meta}PhNC), 7.68 (d, J_{HH} = 8.7 Hz, 2H, H_{ortho}PhNC); (*cis* after irradiation) 7.41 (d, J_{HH} = 8.6 Hz, 2H, H_{meta}PhNC), 6.95 (d, J_{HH} = 8.7 Hz, 2H, H_{ortho}PhNC). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (*trans*) 166.8 (NC), 151.8($C_{q\text{-}N=N)}$, 128.7 (br, C_q-NC), 127.75 (C_{ortho}PhNC), 124.2 (C_{meta}PhNC), IR ($\nu_{(CN)}$): 2127 cm^{-1}. MS (ESI+) m/z: {[CN(C_6H_4)-N=N-(C_6H_4)NC]+H^+}$^+$, 233.08 (*calc.* 233.07). UV-vis [λ_{max}, nm (ε, M^{-1} cm^{-1})] (toluene) 327 (24850), 342 sh (20500), 452 (760); (methanol) 335 (24850), 351 sh (20570), 452 (620). CV (Acetonitrile, *vs* NHE, ferrocene reference): -580, -1020 mV.

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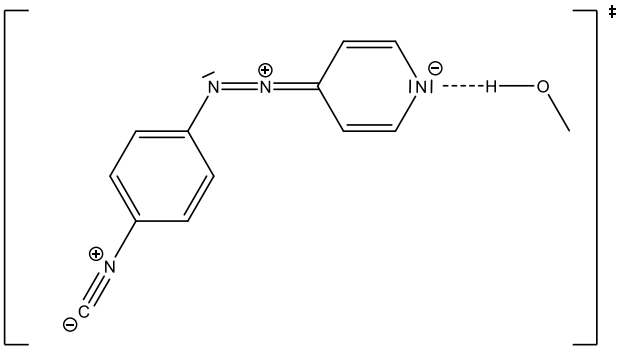


Scheme S1.- Proposed charge-separated transition state for the *cis*-to-*trans* spontaneous process on the $CN(C_6H_4)$-N=N-(C_5H_4N) ligand in methanol solution.

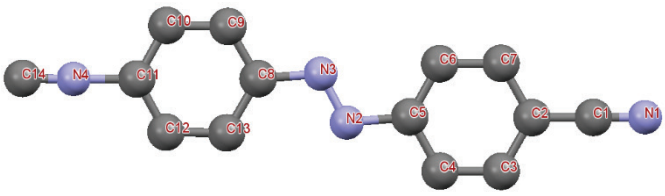


Figure S1.- Ball and stick plot of the XRD structure of the compound $CN(C_6H_4)$-N=N-$(C_6H_4)CN$ (Hydrogen atoms have been omitted for clarity).

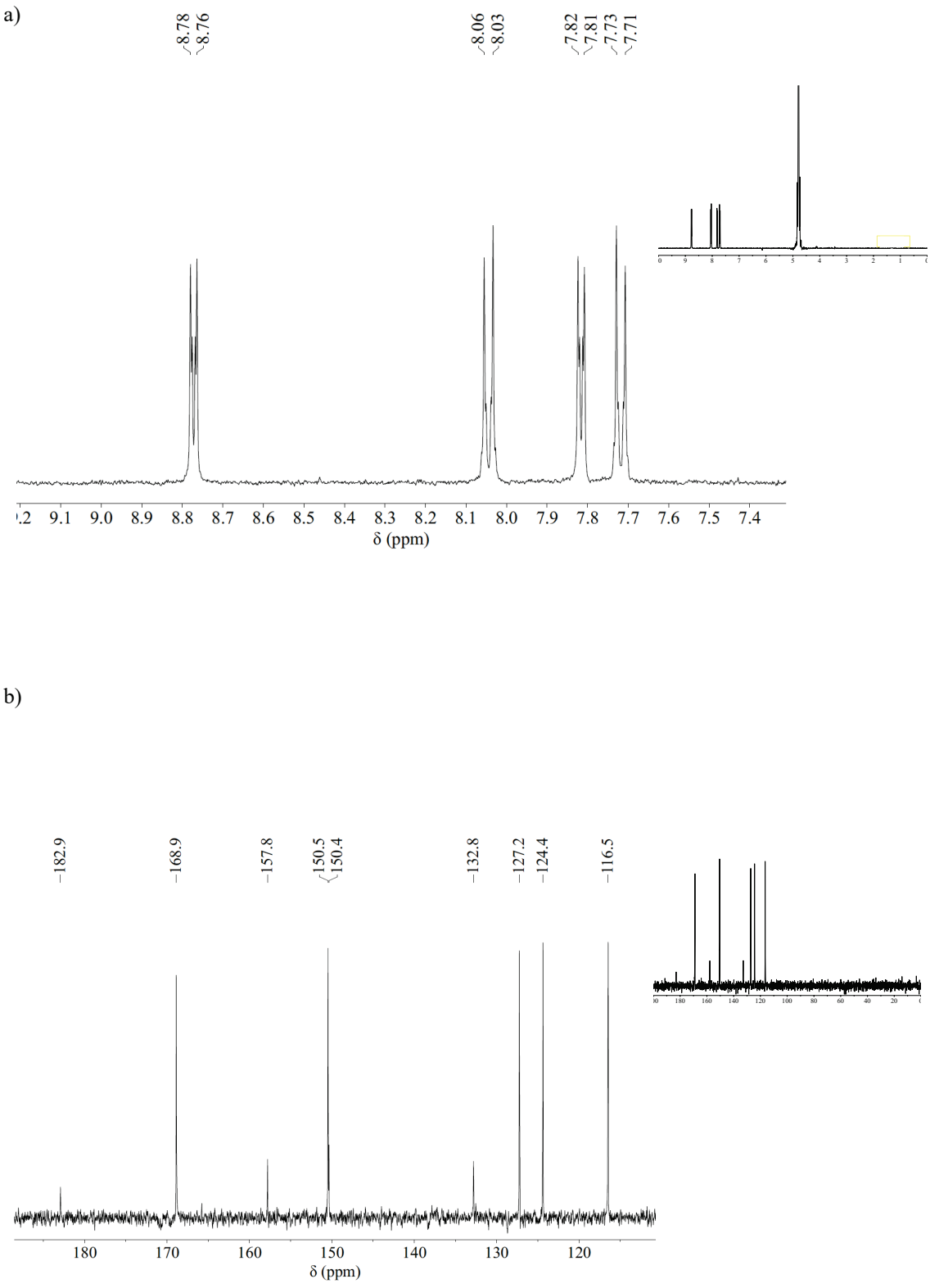


Figure S2.- a) ^{1}H and b) ^{13}C NMR (D_2O) spectra of $Na_3[(NC)_5Fe^{II}CN(C_6H_4)\text{-}N{=}N\text{-}(C_5H_4N)]$ (**py-isoFe^{II}**).

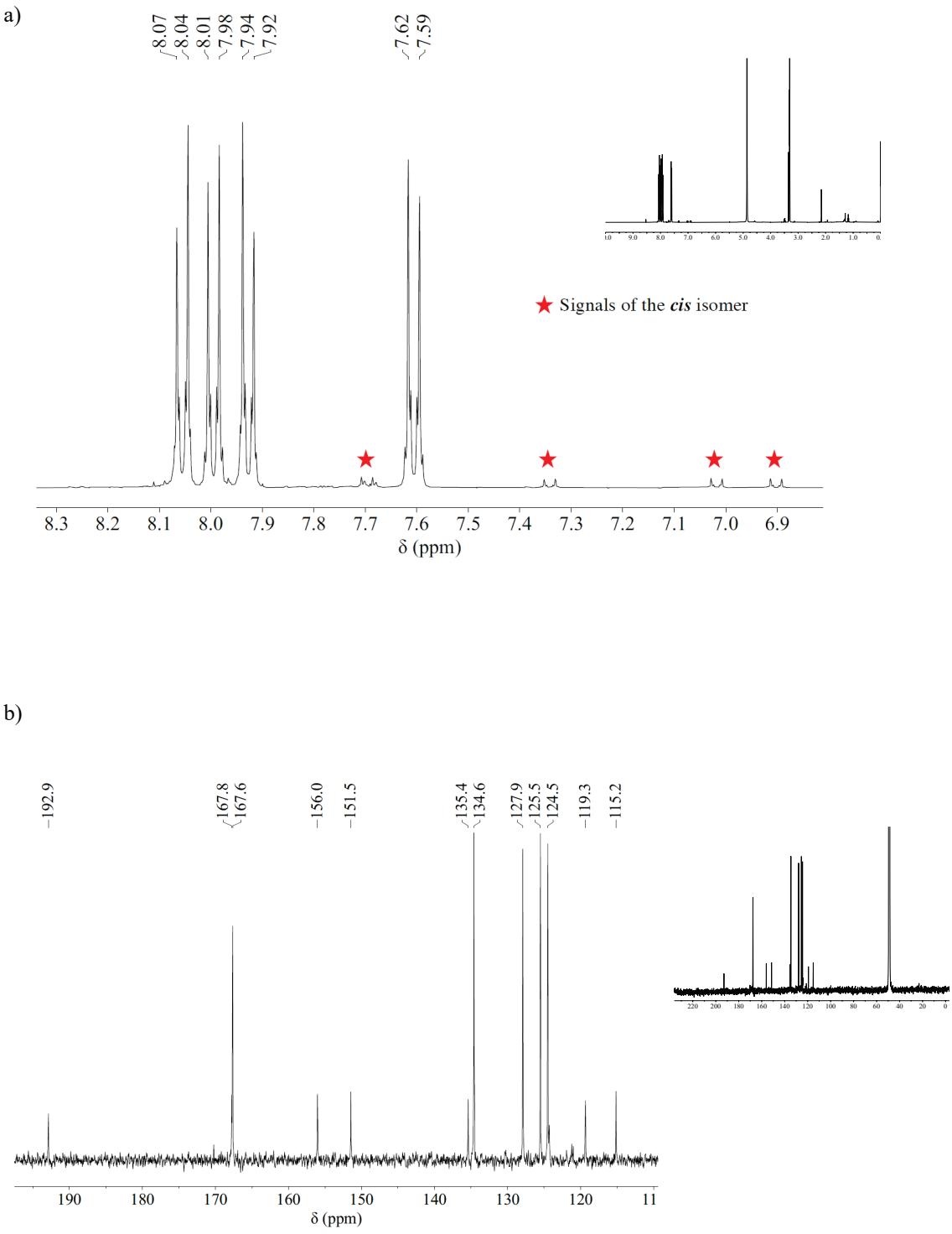
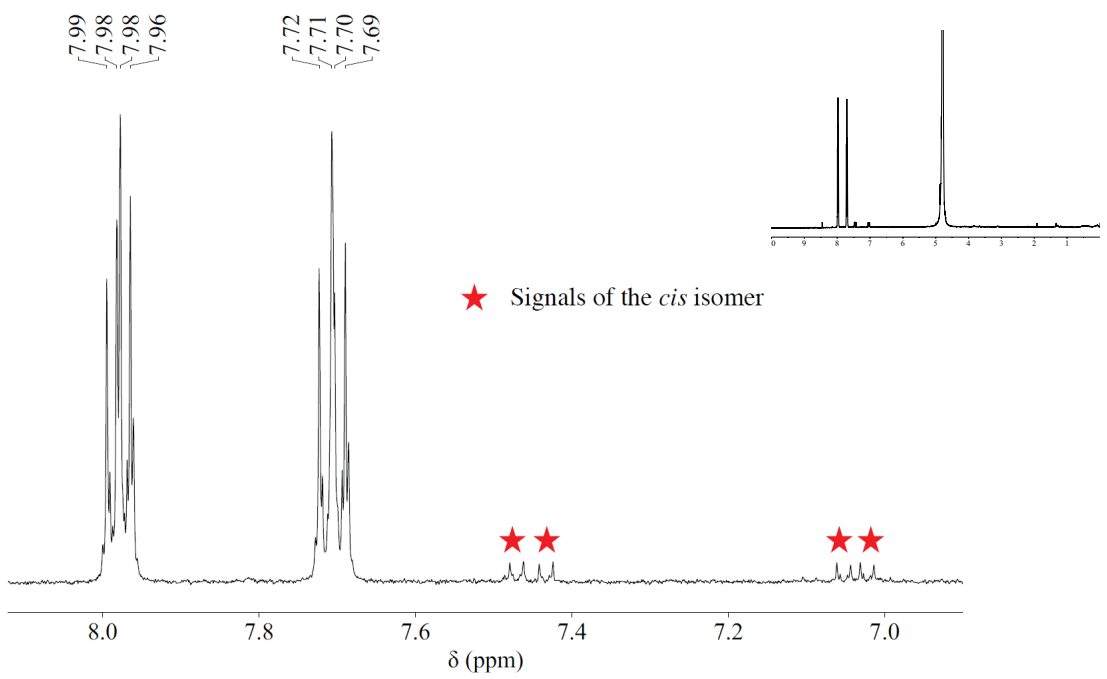


Figure S3.- a) ^{1}H and b) ^{13}C NMR (CD_3OD) spectra of $Na_3[(NC)_5Fe^{II}CN(C_6H_4)$-N=N-$(C_6H_4)CN]$ (**cyano-isoFe^{II}**).

a)



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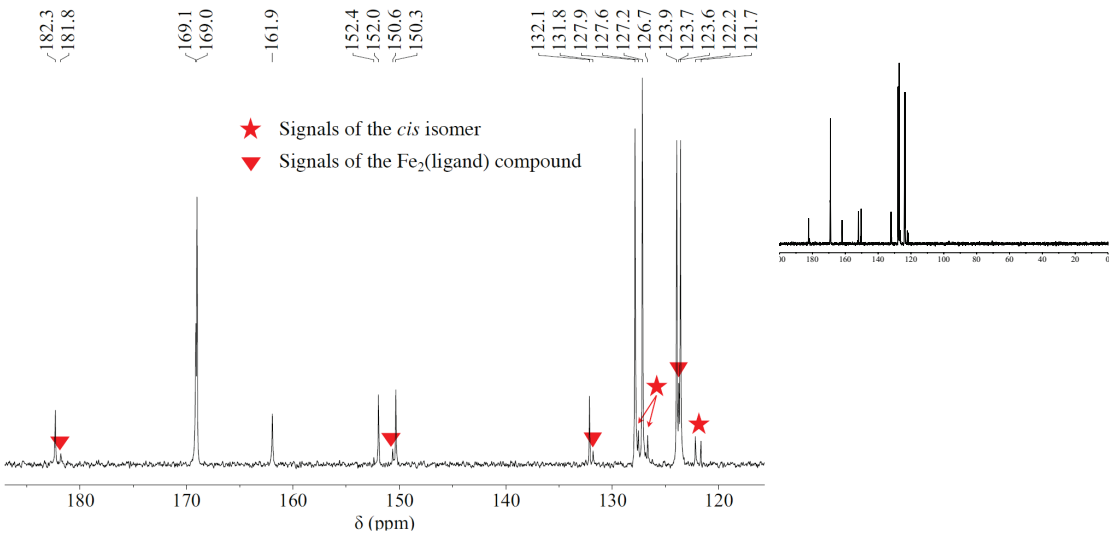
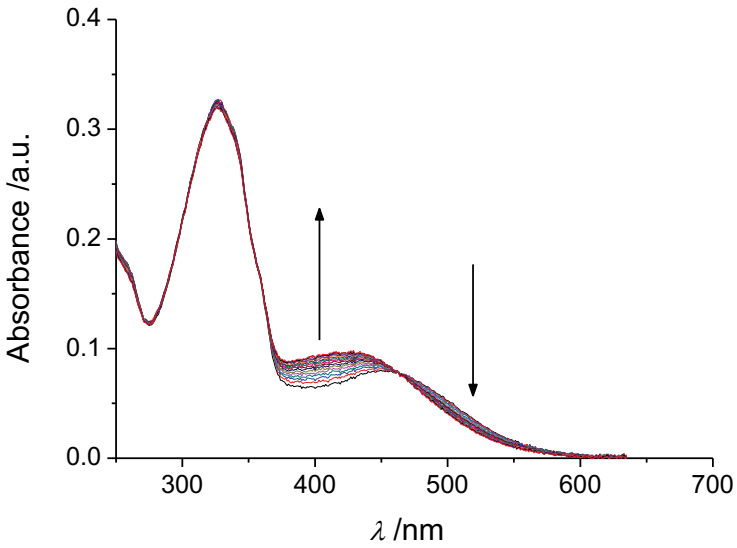


Figure S4.- a) ^{1}H and b) ^{13}C NMR (D_2O) spectra of $Na_3[(NC)_5Fe^{II}CN(C_6H_4)\text{-}N{=}N\text{-}(C_6H_4)NC]$ (**iso-isoFe^{II}**).

a)



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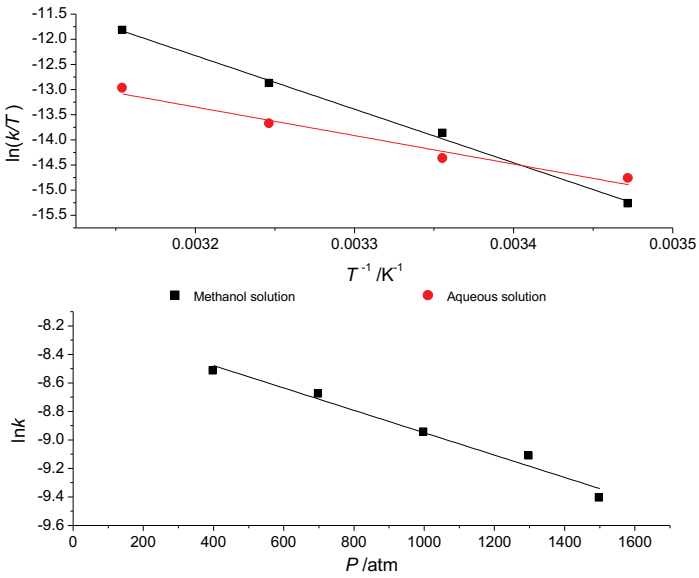


Figure S5.- a) Typical UV-Vis spectral changes observed after irradiation of a methanol solution of $Na_3[(NC)_5Fe^{II}CN(C_6H_4)\text{-}N{=}N\text{-}(C_6H_4)CN]$ at 15 ºC and b) Eyring (top) and ln*k versus P* (bottom) plots obtained from the variation of the observed rate constants in aqueous an methanol solutions of the same compound.

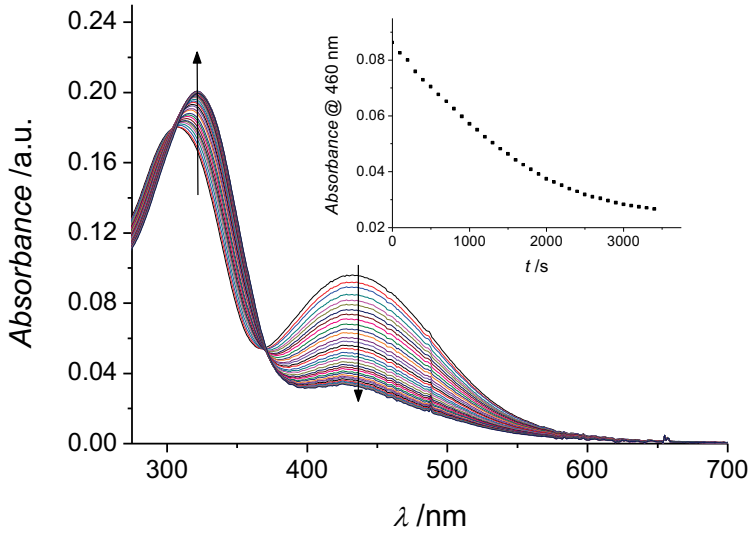
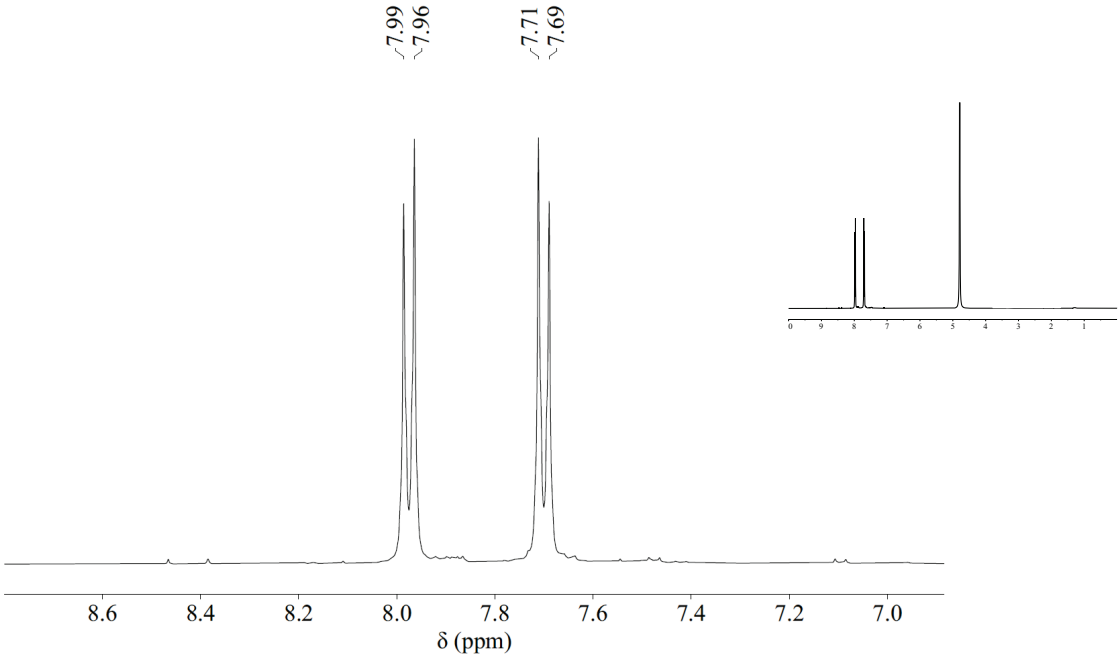


Figure S6.- UV-Vis spectral changes observed for the reaction of $[(NC)_5Fe^{II}CN(C_6H_4)\text{-}N{=}N\text{-}(C_5H_4N)]^{3-}$ with $S_2O_8^{2-}$. $[Fe^{II}] = 1\times10^{-5}$ M, $[S_2O_8^{2-}] = 1\times10^{-3}$ M, I =0.2 M ($NaClO_4$); T = 45 ºC.

a)



b)

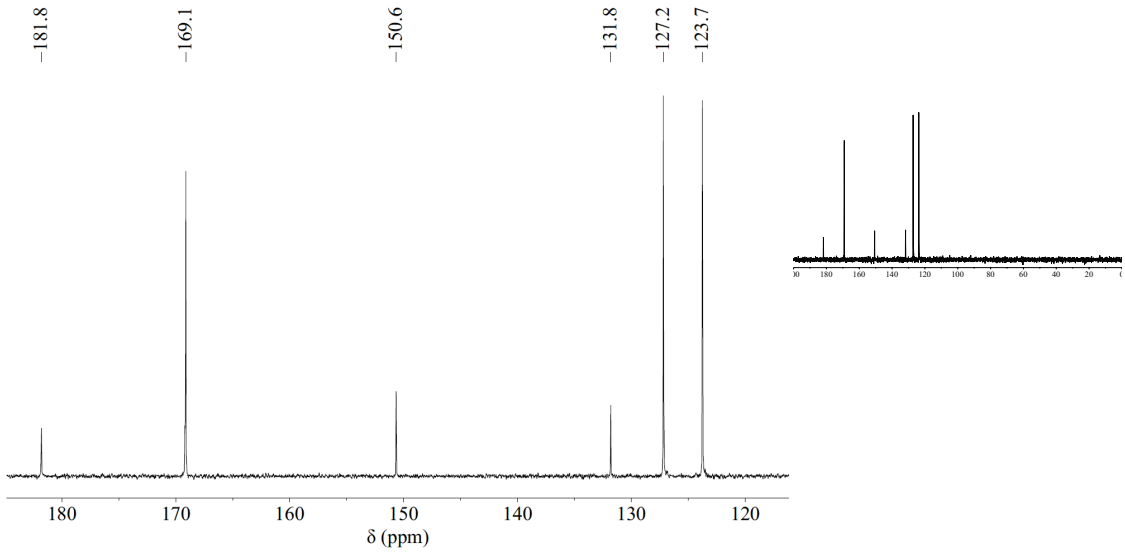
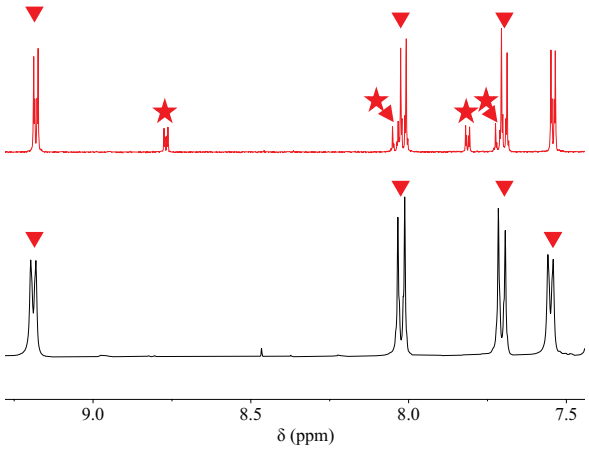


Figure S7.- a) ^{1}H and b) ^{13}C NMR (D_2O) spectra of $Na_6[(NC)_5Fe^{II}CN(C_6H_4)\text{-}N{=}N\text{-}(C_6H_4)NCFe^{II}(CN)_5]$ (**Fe^{II}iso-isoFe^{II}**).

a)



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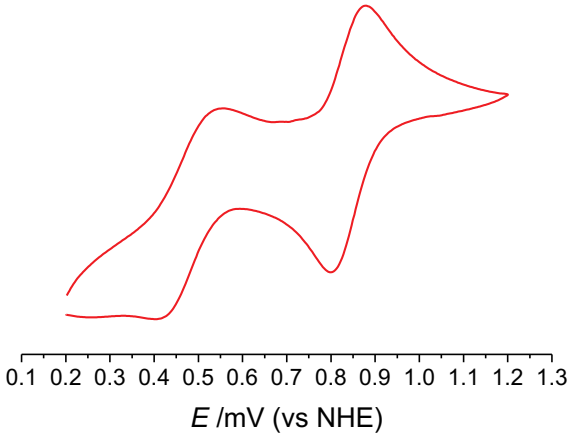

c)

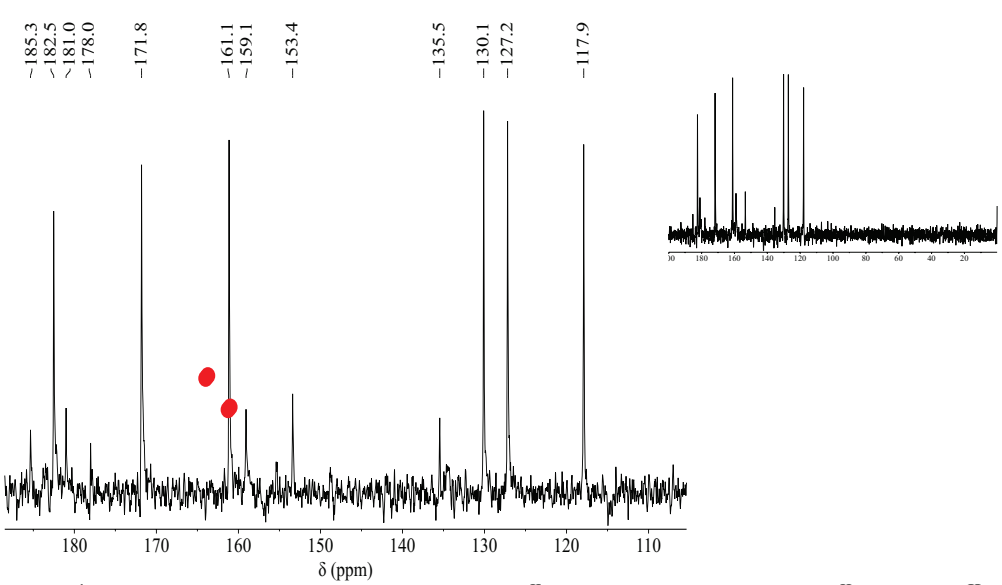

Figure S8.- a) ^{1}H NMR (D_2O) spectrum of $Na_6[(NC)_5Fe^{II}CN(C_6H_4)\text{-}N{=}N\text{-}(C_5H_4N)Fe^{II}(CN)_5]$ (**Fe^{II}py-isoFe^{II}**), immediately after dissolution (black) and after two hours (red, stars correspond to the signals of the $Na_3[(NC)_5Fe^{II}CN(C_6H_4)\text{-}N{=}N\text{-}(C_5H_4N)]$ compound). b) CV of $Na_6[(NC)_5Fe^{II}(NC_5H_4)\text{-}N{=}N\text{-}(C_6H_4)NCFe^{II}(CN)_5]$ immediately after dissolution in water. c) ^{13}C NMR (D_2O) spectra of $Na_6[(NC)_5Fe^{II}CN(C_6H_4)\text{-}N{=}N\text{-}(C_5H_4N)Fe^{II}(CN)_5]$ (red dots indicate the presence of the $[Fe(CN)_5(H_2O)]^{3-}$ compound).

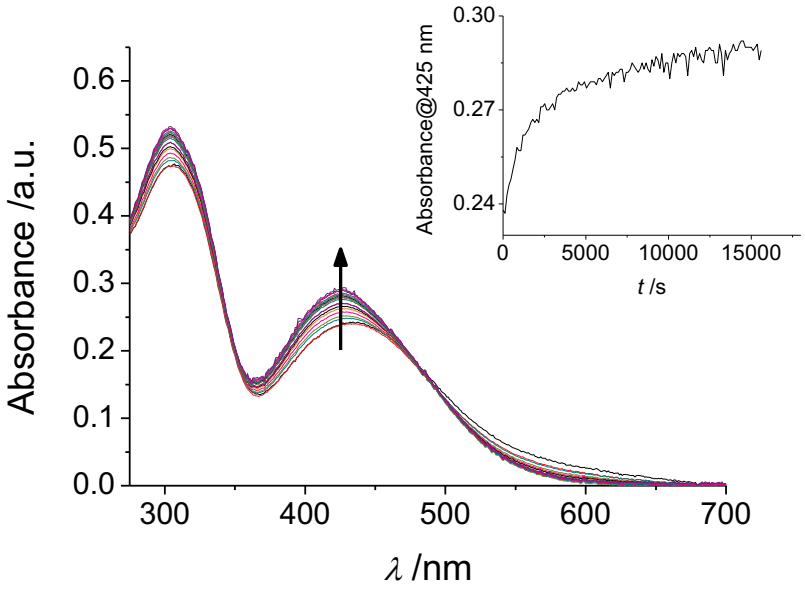

Figure S9.- Time-resolved UV-Vis spectral changes observed on dissolution of the complex $Na_6[(NC)_5Fe^{II}(NC_5H_4)$-N=N-$(C_6H_4)NCFe^{II}(CN)_5]$ in water at 35 ºC.

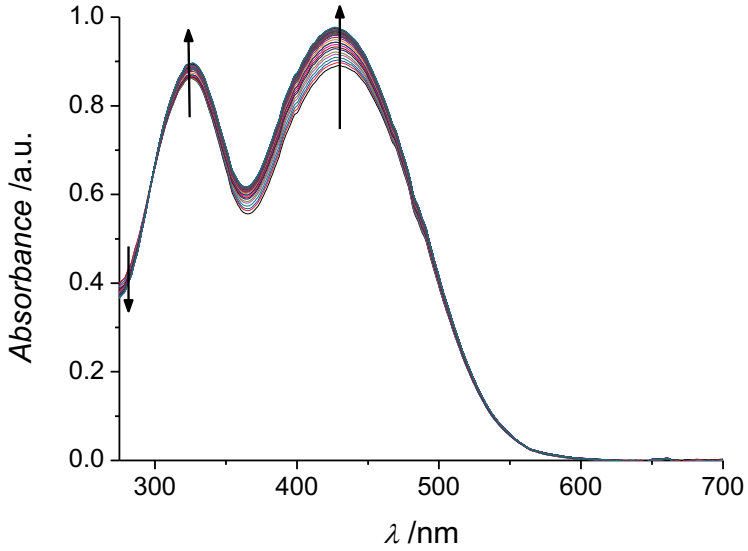

Figure S10.- UV-Vis spectral changes observed after irradiation of a methanol 4×10^{-5} M solution of $Na_6[(NC)_5Fe^{II}CN(C_6H_4)$-N=N-$(C_6H_4)NCFe^{II}(CN)_5]$ at 45 ºC at 1300 atmospheres, total time 3 hours.

Table S1.- Values of the observed 1st-order rate constants for the spontaneous *cis*-to-*trans* isomerisation reaction occurring on the compounds prepared as a function of solvent, temperature and pressure ([compounds] at the 10 μM level; value shown corresponds to the average of two or three replicates with an error within the 10-15 % margin).

Compound	Solvent	T /ºC	P /atm.	$10^3 \times k_{obs}$ /s^{-1}
py-iso	Toluene	25	1	0.030
		40	1	0.11
		55	1	0.50
	Methanol	23	1	0.094
		35	1	0.30
		40	300	0.75
			600	1.0
			900	1.3
			1200	2.0
			1500	2.3
		45	1	0.56
		56	1	1.2
cyano-iso	Toluene	25	1	0.0097
		35	1	0.028
		44	1	0.11
		50	1	0.19
		57	1	0.45
	Methanol	25	1	0.0083
		35	1	0.022
		44	1	0.13
		48	300	0.092
			700	0.095
			1100	0.095
			1500	0.092
		50	1	0.21
		57	1	0.37
iso-iso	Toluene	30	1	0.020
		39	1	0.055
		51	1	0.30
		60	1	0.63
	Methanol	30	1	0.018
		39	1	0.040
		51	1	0.20
		60	1	0.48
			400	0.42

			700	0.40
			1000	0.38
			1300	0.40
py-isoFe^{II}	Methanol	15	1	0.045
		25	1	0.090
			400	0.090
			700	0.20
			1000	0.22
			1300	0.18
		35	1	0.31
		45	1	1.0
	Water	15	1	0.075
		25	1	0.18
		35	1	0.60
			400	0.88
			700	0.92
			1000	0.67
			1300	0.71
			1600	1.0
		45	1	1.5
cyano-isoFe^{II}	Methanol	25	1	0.28
			400	0.020
			700	0.017
			1000	0.013
			1300	0.011
			1600	0.0082
		35	1	0.78
		44	1	2.3
	Water	15	1	0.011
		25	1	0.017
		35	1	0.035
		44	1	0.073
		15	1	0.067
iso-isoFe^{II}	Methanol	20	1	0.25
		35	1	0.75
		45	1	1.1
		51	1	1.3
	Water	20	1	0.14
		25	1	0.21
		35	1	0.40

			400	0.45
			700	0.48
			1000	0.52
			1300	0.57
			1600	0.62
		45	1	0.73
		51	1	1.4
py-isoFe^{III}	Water	15	1	0.091
		25	1	0.40
		30	400	0.64
			700	0.53
			1000	0.45
			1300	0.37
			1450	0.33
			1600	0.29
		35	1	1.2
		45	1	2.8
Fe^{II}iso-isoFe^{II}	Water	30	1	0.12
		40	1	0.27
		45	400	0.47
			700	0.50
			1000	0.45
			1300	0.43
			1600	0.45
		50	1	0.69
		60	1	1.5

Table S2.- Values of the observed order rate constants for the peroxodisulfate oxidation reaction of the **py-isoFe^{II}** compound in aqueous solution as a function of temperature and pressure ([**py-isoFe^{II}**] at the 10 μM level, I = 0.20 M $NaClO_4$).

$10^3\times[S_2O_8^{2-}]$ /M	T /ºC	P /atm.	$10^4\times k_{obs}$ /s^{-1}
0.50	15	1	0.080
1.0			0.23
2.0			0.33
3.0			0.52
4.0			0.967
5.0			0.92
1.0	25	1	0.44
2.0			1.1
3.0			1.6
4.0			2.2
5.0			2.9
5.0	30	400	9.0
		550	8.7
		700	13
		900	15
		1000	15
		1100	17
		1200	25
		1300	23
0.50	35	1	0.90
1.0			1.3
2.0			2.6
3.0			3.7
4.0			4.9
5.0			7.0
0.50	45	1	1.4
1.0			2.7
2.0			4.8
3.0			7.2
4.0			10
5.0			12