Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Iron-Catalyzed Electrochemical C-H Perfluoroalkylation of Arenes

Mikhail Khrizanforov,[a] Sofia Strekalova,[a] Vera Khrizanforova,[a] Valeriya Grinenko,[a] Kirill Kholin,[a] Marsil Kadirov[a], Timur Burganov[a], Aidar Gubaidullin[a],
Tatyana Gryaznova,[a] Oleg Sinyashin,[a] Long Xu,[b] David A. Vicic,[b] Yulia Budnikova

[a] A.E.Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, 8, Arbuzov str., 420088 Kazan, Russian Federation Tel.: +7(843)279-53-35; fax: +7(843)275-22-53.
E-mail: yulia@iopc.ru

[b] Department of Chemistry, Lehigh University, 6 East Packer Avenue, Bethlehem, Pennsylvania 18015, United States

Experimental

General Procedures

All reactions were carried out under dry argon atmosphere. All solvents employed were purified and dried prior to use. N,N-Dimethylformamide was purified by double fractionation distillation over melting potash. Perfluoroiodohexane were purchased from P&M Invest and used without further purification. Caffeine, benzene, o-xylene, p-xylene, naphthalene were procured from Acros Organics. Tetraethylammonium tetrafluoroborate was purchased from Aldrich and recrystallized from diethylether. $FeCl_2$ (99.5 %), $FeCl_3*6H_2O$ (97 %) and 2,2'-bipyridine (99+%, all from Alfa Aesar) were used without further purification. Preparative electrolysis were performed by means of the direct current source B5–49 in thermostatically controlled cylindrical divided 100 mL electrolyser (a three-electrode cell). Platinum with surface areas of 20 cm^2 was used as a cathode; platinum rod was used as the anode. The working electrode potential was determined using reference electrode Ag/AgCl. During electrolysis, the electrolyte was stirred with a magnetic stirrer. A saturated solution of Et_4NBF_4 in DMF was used as anolyte, and the anode compartment was separated by a ceramic membrane. Mass spectra were recorded in EI mode using ThermoQuest TRACE MS. IR spectra of the compounds were recorded on a FTIR spectrometer ''Vector 22'' (Bruker) in the 400–4000 cm^{-1} range and on a FTIR spectrometer IFS 113v (Bruker) in the 100–600 cm^{-1} range at a resolution of 1 cm^{-1}. Solid samples were prepared as KBr, respectively.
Raman spectra were registered at room temperature on a BRUKER RAM II module (using a Ge detector operating at liquid nitrogen temperature) attached to a BRUKER VERTEX 70 FTIR spectrometer in the range 10-4000 cm^{-1} with an optical resolution of 4 cm^{-1}. Raman scattering radiation was collected in a back-scattering configuration. 1024 scans were averaged for each spectrum. A Nd:YAG laser with a wavelength of 1064 nm and power of 150-250 mW was used as the excitation source. The samples were inserted in a standard glass cell.

Powder X-ray diffraction (PXRD) measurements for structural analyses were performed on a Bruker D8 Advance diffractometer equipped with Vario attachment and Vantec linear PSD, using Cu radiation (40 kV, 40 mA) monochromated by the curved Johansson monochromator (λ Cu $K_{\alpha 1}$ 1.5406 Å). Room-temperature data were collected in the reflection mode with a flat-plate sample. The samples were loaded on a standard zero diffraction silicon plate, which was kept spinning (15 rpm) throughout the data collection. Patterns were recorded in the 2Θ range between 3° and 90°, in 0.008° steps, with a step time of 0.3–5.0s. Several diffraction patterns in various experimental modes were collected and summed for the sample. Processing of the obtained data performed using EVA [DIFFRAC Plus Evaluation package EVA, Version 11 (2005). User's Manual, Bruker AXS, Karlsruhe. Germany. - 258 p] software packages.

NMR experiments

NMR investigation was carried out in the NMR department (A.E. Arbuzov Institute of Organic and Physical Chemistry) of the Federal Collective Spectral Analysis Center for physical and chemical investigations of structure, properties and composition of matter and materials. NMR experiments were carried out with Bruker spectrometers AVANCE-400 (400.1 MHz (1H), 376.5
MHz (^{19}F), 100.6 MHz (^{13}C)) and AVANCE-600 (600.1 MHz (1H), 150.9 MHz (^{13}C) equipped with a pulsed gradient unit capable of producing magnetic field pulse gradients in the z-direction of 53.5 G cm^{-1}. All spectra were acquired in a 5 mm gradient inverse broad band probe head. Chemical shifts are reported in the δ (ppm) scale relative to the residual ^1H and ^{13}C signal of C_6D_6, to external C_6F_6 (-164.9 ppm) for ^{19}F NMR spectra.

ESR experiments

Oxygen was removed from liquid samples by three cycles of "freezing in liquid nitrogen—evacuation—thawing" and after the last cycle the electrolysis cell was filled with gaseous helium. The material of the auxiliary electrode was platinum, the reference electrode was Ag/AgCl equipped with a bridge of a carbon slatepencil, and a gold wire 0.5 mm in diameter served as a working electrode. Electrochemical experiments were carried out in DMF at 293 K using 0.1 M Bu_4NBF_4 as a supporting electrolyte; the potential sweep E(t) being 0.1 V s^{-1}. In experiments with spin trap, an equimolar to Fe complex amounts of N-Tert-butyl-α-phenylnitrone (PBN) was added to solution. The measurements were carried out on an apparatus program complex including an analog electrochemical system with a potentiostat and a PWR-3 programmer, an ELEXSYS E500 ESR spectrometer of the X-range, and an E14-440 analog-to-digital and digital-to-analog modulus (L-Card), a fourth-generation computer, and a unique three-electrode helical cell [1-2]. ESR spectra were simulated using the WinSim 0.96 program (developed by NIEHS).

Synthesis of iron-bpy complexes

Synthesis of [(bpy)FeCl$_3$]

[(bpy)FeCl$_3$] was prepared using the method of Ocafrain [3] and according to the following procedure substituting DMF for ethyl alcohol as solvent (the product was identical):

2,0 g (7,39 mmol) of hexa-hydrate $FeCl_3$ was entirely dissolved in 100 mL of ethanol and then a solution of 1,15 g (39 mmol) of 2,2'-bipyridine in 100 mL of ethanol was added dropwise (during approximately 10 min) to the stirred solution of $FeCl_3$*H_2O at room temperature. After all of the bpy/ethanol solution had been added, the stirring had been continued during 24 hours. After that the orange precipitate was filtered and washed first with two 20 mL portions of glacial ethanol and second with one 10 mL portions diethyl ether. Drying the precipitate under vacuum (-10 torr) at room temperature (t= 23 °C) produced an orange powder. The observed yield was 86% (2,04 g). Found, (%) :C: 37,65; H: 2,47; N: 8,81. C10H8Cl3FeN2. Calculated, (%):C, 37.72; H, 2.53; Cl, 33.41; Fe, 17.54; N, 8.80.

Features of **[(bpy)FeCl$_3$]** coincide with the literature data [4].

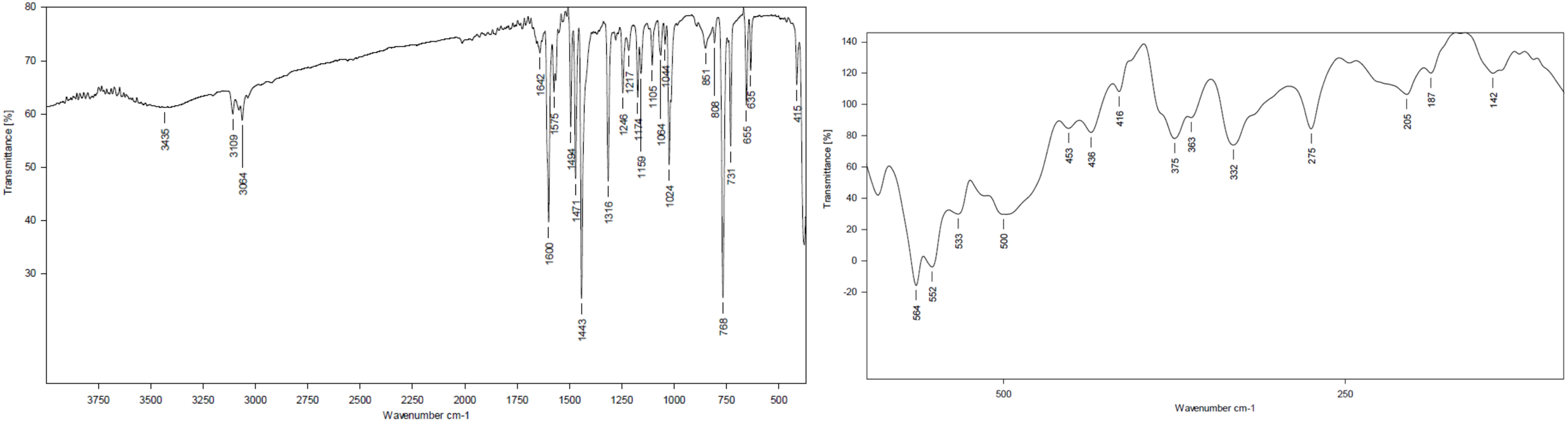


Figure.1S. IR spectra of [(bpy)FeCl$_3$]

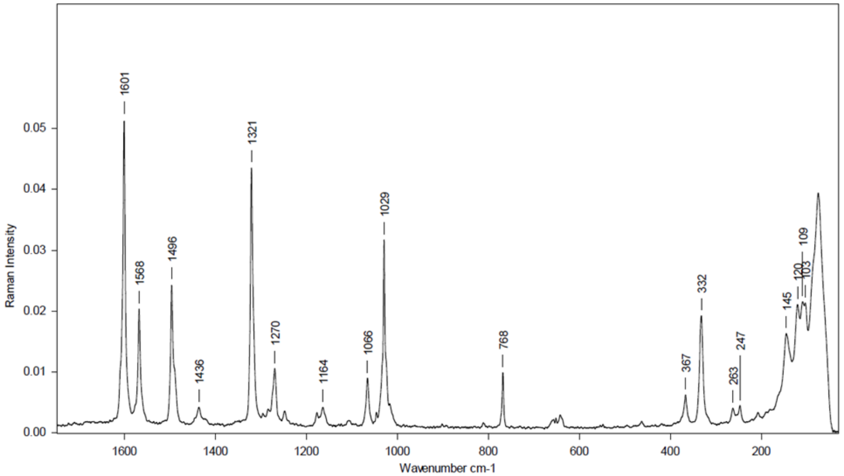


Figure.2S. Raman spectrum of [(bpy)FeCl$_3$]

Synthesis of [(bpy)FeCl$_2$]

We synthesized [(bpy)FeCl$_2$] originally using the method of Dwyer [5], The same method was used by W. M. Reiff in 1975 [6]. Rose-red powder was obtained. Then we used our own method, which gave the powder with exactly the same properties. Our synthesis procedure is following:

The red-rose isomer of Fe(bpy)Cl$_2$ complex was synthesized under an atmosphere of nitrogen gas to ensure that the Fe(II) cation was not oxidized during the reaction. Once the 2,0g (15,8 mmol) of pale green ferrous chloride powder was entirely dissolved in 100 mL of ethanol and then a deoxygenated solution of 1.75g (11.06 mmol) of 2,2'-bipyridine in 100 mL of ethanol was added dropwise (during approximately 10 min) to the stirred solution of FeCl$_2$ at room temperature. The 0.7/1 bpy/Fe molar ratio was used to favor the formation of the mono-2,2'-bipyridine complex [Fe(bpy)Cl$_2$], over the bis or tris complex. As soon as a few milliliters of the transparent, colorless bpy/ethanol solution had been combined with the clear, light green FeCl$_2$/ethanol solution, the color of the reaction mixture became bright red. As the addition of the bpy/ethanol solution proceeded, the color of the reaction mixture practically wasn't changed. After all of the bpy/ethanol solution had been added, the stirring was continued for another 24 hours to be sure that the reaction was completed. Then stirring has been stopped, the product (a red precipitate) was filtered and was washed first with two 20 mL portions of glacial ethanol and second with one 10 mL portions of diethyl ether. Drying the precipitate under vacuum (-10 torr) at room temperature (t=23 °C) produced a red-rose powder. The observed yield was 85% (2,7 g). 1H (C6D6, d,ppm, J/Hz): 8.55 (s, 2H, 3 and 3' vs. N), 8.14 (s, 2H, 6 and 6' vs. N), 7.44 (s, 4H, 4,4',5,5' vs. N). Found, (%) :C: 42,36; H: 2,82; N: 9,92. C10H8Cl2FeN2. Calculated, (%): C, 42.45; H, 2.85; Cl, 25.06; Fe, 19.74; N, 9.90.

Features and spectra (IR, Raman, X-ray powder diffraction, elemental analysis) correspond to those for rose-red complex of [(bpy)FeCl$_2$] described by Sato [7], Reiff [6] and Dwyer [5], although the resolution of the old literary spectra is bad, and are different from the data for the orange polymorph [8,9].

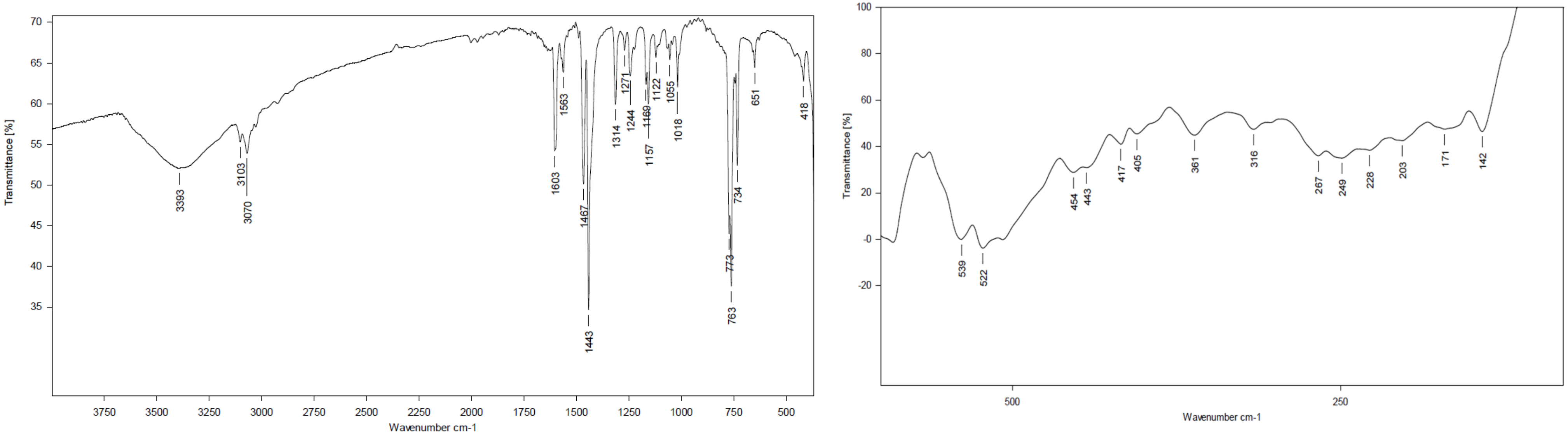


Figure 3S. IR spectra of [(bpy)FeCl$_2$]

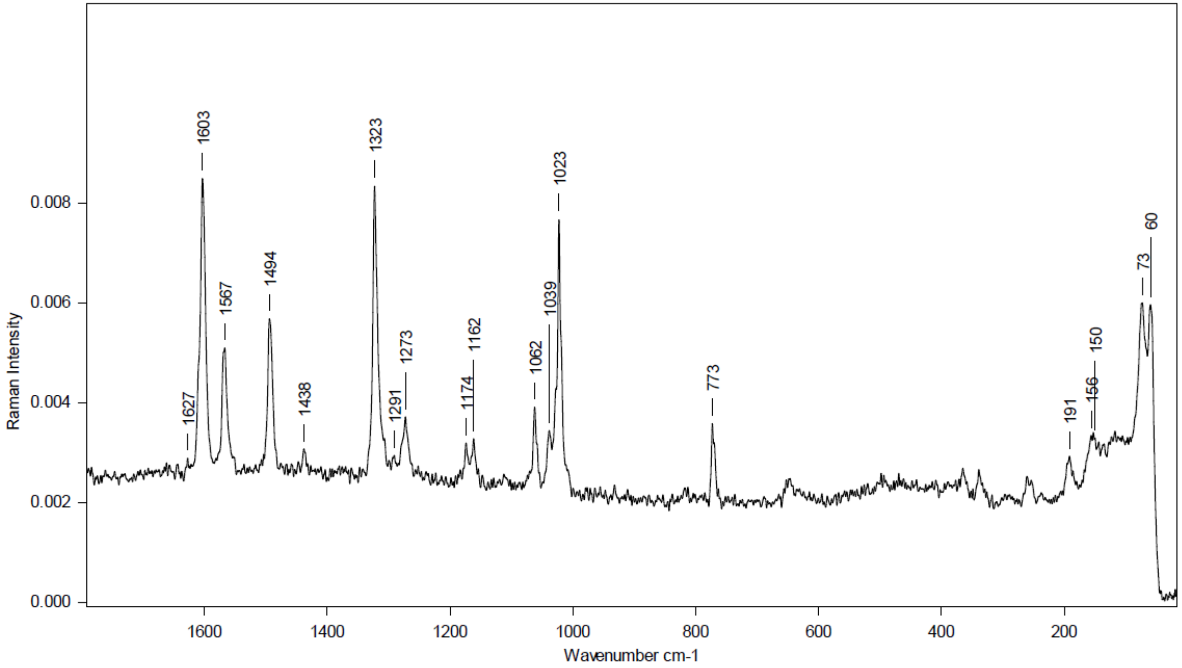


Figure 4S. Raman spectrum of [(bpy)FeCl$_2$] (solid).

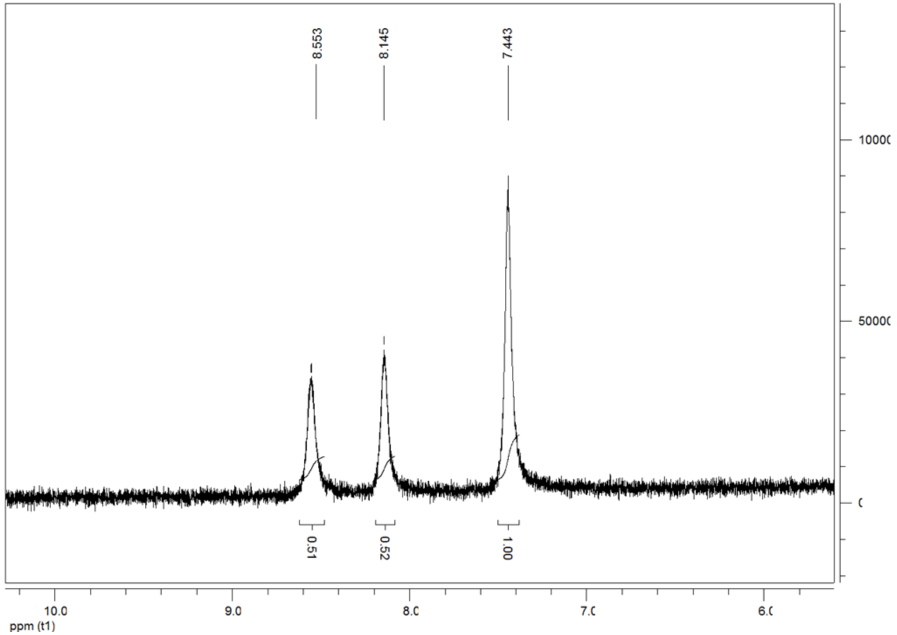


Figure 5S. ^{1}H NMR spectrum of [(bpy)FeCl$_2$] in CD$_3$CN .

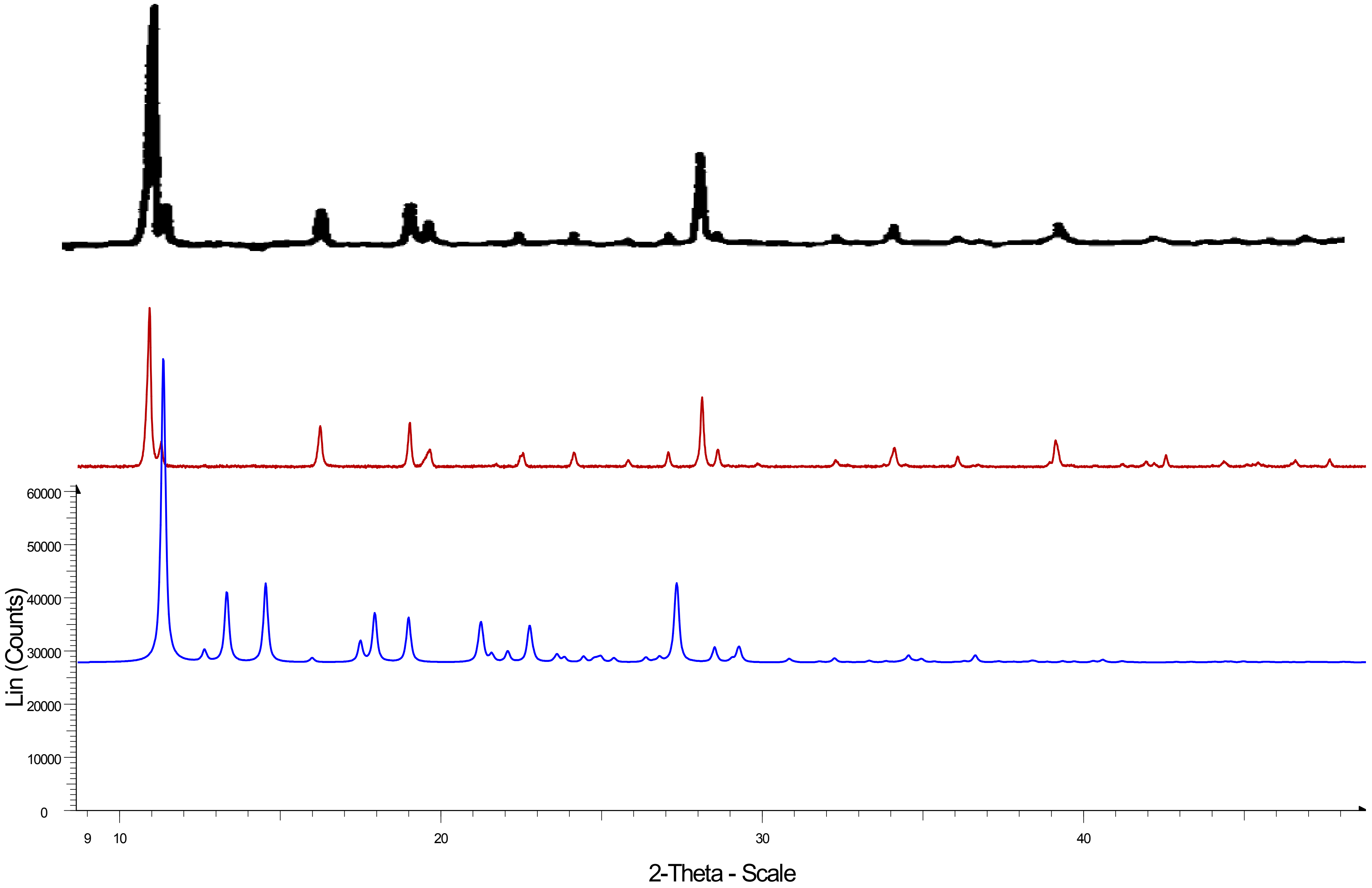


Figure 6S. Experimental X-ray powder pattern for rose-red [(bipy)FeCl$_2$] sample (red curve), theoretical XRD curve for orange Fe(bipy)Cl$_2$ sample calculated on the basis of the unit cell parameters and coordinates of the atoms obtained from XRD data in the paper of Lapidus-Miller [9] (blue curve), and fragment of XRD pattern for rose-red Fe(bipy)Cl$_2$, presented in the work of Sato and colleagues [7] in 1975 (black curves).

The first two curves are coincide practically (despite the poor quality of the data in the [7]), and this gives the grounds to assume that the unit cell parameters and characteristics of the crystal packing in both samples are the same and refer to the red-rose polymer form of a [(bipy)$FeCl_2$] compound. Note the substantial difference between these diffraction patterns obtained for the dimeric orange form of the compound (blue curve). The powder X-ray diffraction data obtained for red-rose form currently used for indexing and decoding the molecular structure of compounds and will be published as they become available.

Electrosynthesis and Synthesis

Perfluorohexylbenzene (1)

Condition 1: A solution for electrolysis was prepared by mixing 0.28 g (1.0 mmol) (bpy)$FeCl_3$, 4.34 g (9.7mmol) perfluoroiodohexane and 1.09 g (9.7 mmol) *t*-BuOK in [DMF:benzene]=[1:1] (50 ml). Electrolysis was carried out in an electrochemical cell with separation of anode and cathode compartments at ambient temperature under argon atmosphere at the potential of a working electrode -1.0 V vs. Ag/AgCl. The amount of electricity passed through the electrolyte were 2F per one mole of perfluoroiodohexane (520 $mA\times h^{-1}$). After completing the electrolysis, the solution was washed with distilled water (100 ml) and extracted with benzene (3×100 ml). The organic layer was dried over magnesium sulfate and filtered. The residual solution was concentrated. The reaction mixture was filtered through a plug of silica (eluated with 5% EtOAc : 95% hexane). The filtrate was concentrated, and the product was isolated as a colorless oil (3.11 g, 81% isolated yield). The spectroscopic data for **1** matched that reported in the literature [10, 11]

Condition 2: Similarly like the condition 1, but in the absence of *t*-BuOK (1.53 g, 40% isolated yield of **1**).

Condition 3: Similarly like the condition 1, but (bpy)$FeCl_2$ 0.28 g, 1.0 mmol was used instead (bpy)$FeCl_3$; (3.07 g, 80% isolated yield of **1**).

Condition 4: Similarly like the condition 3, but in the absence of *t*-BuOK (3.03 g, 79% isolated yield of **1**)

Condition 5 (Chemical): A solution for synthesis was prepared by mixing 0.28 g (1.0 mmol) (bpy)$FeCl_3$, 4.34 g (9.7mmol) perfluoroiodohexane and 1.09 g (9.7 mmol) *t*-BuOK in [DMF:benzene]=[1:1] (50 ml). Synthesis was carried out in an round-bottomed flask at ambient temperature. Before starting the reaction, the reaction mixture was purged with argon, then tightly stoppered. The synthesis was performed during 48 hours. After completing the synthesis, the solution was washed with distilled water (100 ml) and extracted with benzene (3×100 ml). The organic layer was dried over magnesium sulfate and filtered. The residual solution was concentrated. The reaction mixture was filtered through a plug of silica (eluated with 5% EtOAc : 95% hexane). The filtrate was concentrated, and the product was isolated as a colorless oil (0.26 g, 7% isolated yield of **1**).

Condition 6: Similarly like the condition 5, but in the absence of *t*-BuOK (no product).

Condition 7: Similarly like the condition 5, but stoichiometric quantity 2.72 g (9.7mmol) (bpy)$FeCl_3$ was used. (2.41 g, 63% isolated yield of **1**)

Condition 8: Similarly like the condition 7, but in the absence of *t*-BuOK (no product).

Condition 9: Similarly like the condition 5, but (bpy)$FeCl_2$, 0.28 g (1.0 mmol) was used instead (bpy)$FeCl_3$. (2.11 g, 55% isolated yield of **1**)

Condition 10: Similarly like the condition 9, but in the absence of *t*-BuOK (no product).

Condition 11: Similarly like the condition 9, but used stoichiometric quantity 2.74 g (9.7mmol) (bpy)$FeCl_2$. (3.03 g, 79% isolated yield)

Condition 12: Similarly like the condition 11, but in the absence of *t*-BuOK (0.27 g, 7% isolated yield of **1**).

1-(Perfluorohexyl)naphthalene (2)

Condition 13: A solution for electrolysis was prepared by mixing 0.28 g (1.0 mmol) [(bpy)$FeCl_3$], 4.34 g (9.7 mmol) perfluoroiodohexane, 1.09 g (9.7 mmol) *t*-BuOK and 1.24 g (9.7 mmol) naphthalene in DMF (50 ml).Electrolysis was carried out in an electrochemical cell with separation of anode and cathode compartments at ambient temperature under argon atmosphere at the potential of a working electrode -1.0 V. The amounts of electricity passed through the electrolyte were 2 F per one mole of 6-H-perfluorobromohexane (520 mA×h^{-1}). After completing the electrolysis, the solution was washed with distilled water (100 ml) and extracted with benzene (3×100 ml). The organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. Residue was purified by column chromatography (SiO2; hexane:EtOAc = 9:1) to afford 1-(perfluorohexyl)naphthalene. The product was isolated as a yellow solid (2.29 g, 53% isolated yield, 5:1 ratio of 1-perfluoroalkyl:2-perfluoroalkyl isomers). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.22(1H, d, J = 8.6 Hz), 8.04 (1H, d, J = 8.2 Hz), 7.93 (1H, d, J = 7.4 Hz), 7.82 (1H, d, J = 7.0 Hz), 7.64-7.49 (3H, m). ^{19}F NMR (376 MHz, $CDCl_3$): δ = –80.84 (3F, t, J = 9.9 Hz), –104.51 (2F, t, J = 14.5 Hz), –120.19 (2F, br. s.), –121.14 (2F, br. s.),–122.53 (2F, br. s.), –126.07 (2F, br. s.). IR (KBr, ν ,cm^{-1}) 1140, 1208, 1241 (CF_2), 1365 (CF_3), 1601–1507 (naphthalene). EIMS, m/z: 446,08 $[M]^+$. Anal. calc. (%): C 43.07; H 1.58; F 55.35. Found (%): C 43.03; H 1.54.

2-(Perfluorohexyl)naphthalene (2a)

^1H NMR (400 MHz, $CDCl_3$): δ = 8.13 (1H, s), 7.96 (1H, d, J = 3.7 Hz), 7.95-7.89 (2H, m), 7.67-7.52 (3H, m). ^{19}F NMR (376 MHz, $CDCl_3$): δ = –80.74 (3F, t, J = 9.9 Hz), –109.85 (2F, t, J = 14.1 Hz), –121.63 (2F, br. s.), –122.53 (4F, br. s.), –126.10 (2F, br. s.).

Condition 14: Similarly like the condition 13, but in the absence of *t*-BuOK. (0.95 g, 22% isolated yield of 1-(Perfluorohexyl)naphthalene).

Condition 15: Similarly like the condition 13, but instead (bpy)$FeCl_3$ used 0.28 g (1.0 mmol) (bpy)$FeCl_2$. (2.16 g, 50% isolated yield of 1-(Perfluorohexyl)naphthalene).

1,2-Dimethyl-4-(perfluorohexyl)benzene (3)

Condition 16: A solution for electrolysis was prepared by mixing 0.28 g (1.0 mmol) (bpy)$FeCl_3$, 4.34 g (9.7 mmol) perfluoroiodohexane, 1.09 g (9.7 mmol) *t*-BuOK and 1.24 g (9.7 mmol) *o*-xylene in DMF (50 ml). The general procedure was followed (2). 1,2- Dimethyl-4-(perfluorohexyl)benzene was formed in 2.26g (55% yield, >20:1 ratio of 4-perfluoroalkyl:3-perfluoroalkyl isomers.)

^1H NMR (500 MHz, C_6D_6): δ = 7.27 (1H, s), 7.21 (1H, d, J = 7.8 Hz), 6.79 (1H, d, J = 7.8 Hz), 1.81 (3H, s), 1.79 (3H, s). ^{19}F NMR (376 MHz, $CDCl_3$): δ = –80.71 (3F, t, J = 10.2 Hz), –110.43 (2F, t, J =14.3 Hz), –121.35 (2F, br. s.), –122.56 (4F, br. s.), –126.08 (2F, d, J = 10.9Hz). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 138.8, 136.6, 131.7, 130.8, 125.1, 123.2, 114.9, 110.8-107.9, 19.75, 19.73. IR (KBr, ν; cm^{-1}): 1143, 1207, 1235 (C–F), 1601 (C-C aromatic), 3069 (HC). EIMS, m/z: 424.08 $[M]^+$. Anal. calc. (%): C, 39.64; H, 2.14; F, 58.22. Found (%): C, 39.59; H, 2.10.

1,2-Dimethyl-3-(perfluorohexyl)benzene (3a)

^1H NMR (500 MHz, C_6D_6): δ = 7.32 (1H, d, J = 5.0 Hz), 6.88 (1H, d, J = 7.2 Hz), 6.83 (1H, d, J = 7.2 Hz), 2.11 (3H, s), 1.83 (3H, s). ^{19}F NMR (376 MHz, $CDCl_3$): δ = –80.79 (3F, t, J = 10.2 Hz), –106.34 (2F, t, J =14.7 Hz), –121.01 (2F, br. s.),–121.34 (2F, br. s.), –122.21 (2F, br. s.), –126.08 (2F, br. s.).

Condition 17: Similarly like the condition 16, but in the absence of *t*-BuOK (0.90 g, 22% isolated yield of 1,2-Dimethyl-4-(perfluorohexyl)benzene).

Condition 18: Similarly like the condition 16, but instead (bpy)$FeCl_3$ used 0.28 g (1.0 mmol) (bpy)$FeCl_2$. (2.13 g, 52% isolated yield of 1,2-Dimethyl-4-(perfluorohexyl)benzene).

1,4-Dimethyl-2-(perfluorohexyl)benzene (4)

Condition 19: A solution for electrolysis was prepared by mixing 0.28 g (1.0 mmol) (bpy)$FeCl_3$, 4.34 g (9.7 mmol) perfluoroiodohexane, 1.09 g (9.7 mmol) *t*-BuOK and 1.24 g (9.7 mmol) *p*-xylene in DMF (50 ml). The general procedure was followed 2. 1,4- Dimethyl-2-(perfluorohexyl)benzene was formed in 2.05g (50% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.41 (1H, s), 7.29 (1H, d, J = 8.0 Hz), 7.19 (1H, d, J = 8.0Hz), 2.41 (3H, t, J = 3.1 Hz), 2.36 (3H, s). ^{13}C NMR (100.6 MHz, C_6D_6): δ = 137.84, 136.51, 134.58, 134.44, 130.25, 127.67, 118.73-111.89 (m), 21.75, 20.99-20.67 (m). ^{19}F NMR (376 MHz, $CDCl_3$): δ = –80.79 (3F, t, J = 10.6 Hz), –111.10 (2F, br. s.), –119.20 (2F, br. s.), –120.88 (2F, br. s.), –122.56 (2F, br. s.), –126.16 (2F, br. s.). EIMS, m/z: 424.17 $[M]^+$. Anal. calc. (%): C, 39.64; H, 2.14; F, 58.22. Found (%): C, 39.60; H, 2.11.

Condition 20: Similarly like the condition 19, but in the absence of *t*-BuOK. (0.82 g, 20% isolated yield of 1,4-Dimethyl-2-(perfluorohexyl)benzene).

Condition 21: Similarly like the condition 19, but instead (bpy)$FeCl_3$ used 0.28 g (1.0 mmol) (bpy)$FeCl_2$. (1.8 g, 44% isolated yield of 1,4-Dimethyl-2-(perfluorohexyl)benzene).

8-(Perfluorohexyl)caffeine (5)

Condition 22:A solution for electrolysis was prepared by mixing 0.28 g (1.0 mmol) (bpy)$FeCl_3$, 4.34 g (9.7 mmol) perfluoroiodohexane, 1.09 g (9.7 mmol) *t*-BuOK and 1.89 g (9.7 mmol) caffeine in DMF (50 ml). 8-(Perfluorohexyl)caffeine was formed in 4.12g (83% yield), m.p. = 105–107 ºC; ^{1}H NMR (600 MHz, CD_3OD): δ = 4.60 (3H, s), 3.99 (3H, s), 3.52 (3H, s); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 156.8, 152.9, 148.3, 111.8, 34.4,30.1, 28.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -82.4 (3F, tt, J = 10.2, 2.6 Hz), -109.8 (2F, br. s.), -121.9 (2F, br. s.), -122.6 (2F, br. s.), -123.8 (2F, br. s.), -127.1 (2F, br. s.); EIMS, m/z: 512.14 $[M]^+$. Anal. calc. (%): C, 32.83; H, 1.77; F, 48.22; N, 10.94; O, 6.25 Found (%): C, 32.74; H, 1.74; N, 10.93.The spectroscopic data for **5** matched that previously reported [12].

Condition 23: Similarly like the condition 22, but in the absence of *t*-BuOK (2.73 g, 55% isolated yield).

Condition 24: Similarly like the condition 22, but instead (bpy)$FeCl_3$ used 0.28 g (1.0 mmol) (bpy)$FeCl_2$. (4.13 g, 83% isolated yield)

Condition 25: Similarly like the condition 24, but in the absence of *t*-BuOK. (3.77 g, 76% isolated yield)

Condition 26: A solution for synthesis was prepared by mixing 0.28 g (1.0 mmol) (bpy)$FeCl_3$, 4.34 g (9.7mmol) perfluoroiodohexane and 1.09 g (9.7 mmol) *t*-BuOK and 1.89 g (9.7 mmol) caffeine in DMF (50 ml). Synthesis was carried out in an round-bottomed flask at ambient temperature. Before starting the reaction, the reaction mixture was purged with argon, then tightly stoppered. The synthesis was performed 48hours. After completing the synthesis, the solution was washed with distilled water (100 ml) and extracted with benzene (3×100 ml). The organic layer was dried over magnesium sulfate and filtered. The residual solution was concentrated. The reaction mixture was filtered through a plug of silica (eluated with 5% EtOAc : 95% hexane). The filtrate was concentrated, and the product was isolated as a colorless oil (0.39 g, 8% isolated yield).

Condition 27: Similarly like the condition 26, but in the absence of *t*-BuOK. (No product)

Condition 28: Similarly like the condition 26, but used stoichiometric quantity 2.72 g (9.7mmol) (bpy)$FeCl_3$. (3.17 g, 63% isolated yield)

Condition 29: Similarly like the condition 28, but in the absence of *t*-BuOK. (No product)

Condition 30: Similarly like the condition 26, but instead (bpy)$FeCl_3$ used 0.28 g (1.0 mmol) (bpy)$FeCl_2$. (2.82 g, 57% isolated yield)

Condition 31: Similarly like the condition 30, but in the absence of *t*-BuOK. (No product)

Condition 32: Similarly like the condition 30, but used stoichiometric quantity 2.74 g (9.7mmol) (bpy)$FeCl_2$. (4.02 g, 81% isolated yield)

Condition 33: Similarly like the condition 32, but in the absence of *t*-BuOK. (1.09 g, 22% isolated yield).

Cyclic voltammetry

Cyclic voltammograms of all complexes have been recorded in DMF with 0.005 mol×dm^{-3} substrate concentration, Bu_4NBF_4 was used as a supporting electrolyte (0.1 mol× dm^{-3}) and a glassy carbon electrode as a working electrode (8 cm^2), auxiliary electrode was platinum rod. All potentials are referenced against the Ag/AgCl, 10^{-2} M in DMF. Cyclic voltammograms registration was performed with BASi Epsilon potentiostate (USA).

The calculation of the reaction order:

For a reversible electron-transfer reaction followed by a fast catalytic reaction at high substrate concentrations, the ratio between the catalytic current, i_c, and the diffusion current observed for the reduction of the catalyst in the absence of substrates, i_d, is given by eq:

$$\frac{i_c}{i_d} = \frac{\sigma}{0.447}\sqrt{\frac{RT}{nF}}\sqrt{\frac{kC^m}{\nu}}$$

where n is the number of electrons involved in catalyst reduction, k is the rate constant, v is the scan rate, C is the concentration of the substrate (R_fI), and m is an exponent corresponding to the reaction order of the substrate [13-15]. If the catalytic current is proportional to the square root of the concentration of the substrate, the reaction is first order with respect to the substrate, if the current is directly proportional to the substrate concentration, the reaction is the second order with respect to the substrate. If the catalytic current is directly proportional to the concentration of the catalyst, the reaction order of the catalyst is first. Etc. The calculations based on the voltammograms can be in the case for fast regeneration of the catalyst only when the gain in current is significant to minimize the error. If the stage with some reaction partner is slow (the stage of the arene in our reaction) and does not affect the catalytic currents, the calculation of the order of this reagent is impossible.

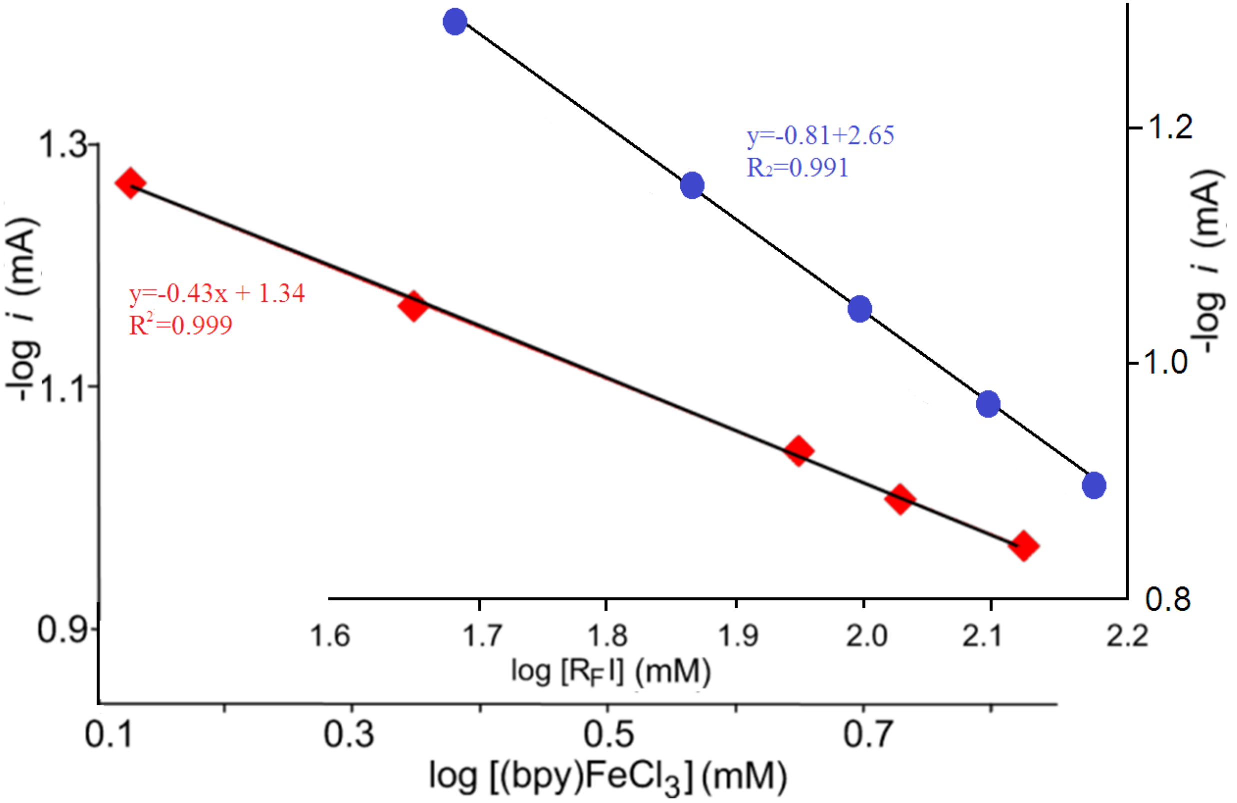
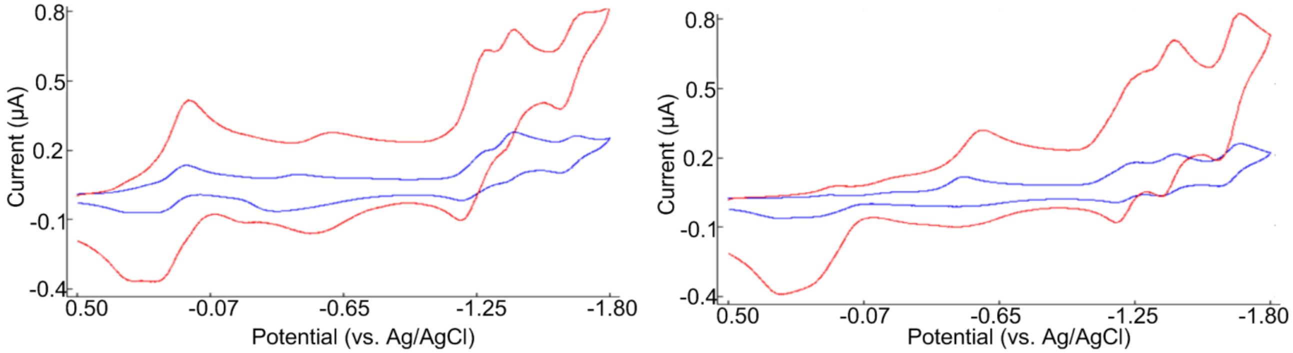


Figure 7S. Plot log i_{cat} vs. –log [(bpy)FeCl$_3$] at constant R$_F$I concentration (blue) (C(R$_F$I)= 30 mM) and Plot log i_{cat} vs. –log [R$_F$I] (red) ([(bpy)FeCl3]=5 mM) (E_p^{cat} = -1.0V vs Ag/AgCl).

($\Delta \log i/\Delta \log$[R$_F$I])/ ($\Delta \log i/\Delta \log$[[(bpy)FeCl$_3$]]) = 2, i.e. the order of the reaction with respect to substrate (R$_F$I) twice as much as the order of the reaction with respect to the catalyst [(bpy)Fe].



a) b)

Fig. 8S CVs of 5 mM [Fe(bpy)] complexes in DMF. **a)** [(bpy)$FeCl_3$] , b) [(bpy)$FeCl_2$]. Conditions: 0.1 V/s scan rate, 0.1 M Bu_4NBF_4, working electrode: glassy carbon (3.0 mm dia.) (red), Au (1.6 mm dia.) (blue).

ESR experiments

All EPR experiments have been performed for $5 \bullet 10^{-3}$ M solution of [(bpy)Fe(III,II)] in the presence or absence 1 equiv. R_fI as substrate, tBuOK as base.

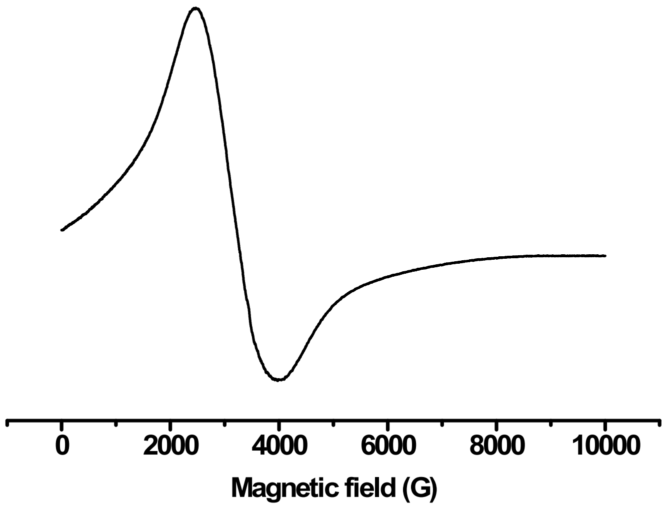


Figure 9S. ESR spectrum of the powder [(bpy)$FeCl_3$] complex at room temperature.

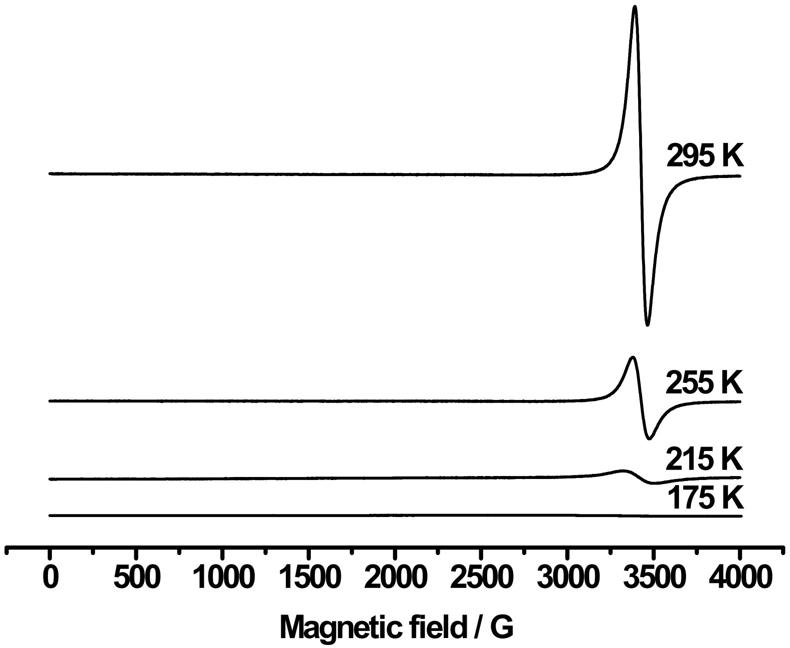


Figure 10S. Temperature dependence of the ESR spectrum of the [(bpy)FeCl$_3$] complex in DMF (g = 2.014, $\Delta H_{\text{pk-pk}}$ = 60 G at room temperature)

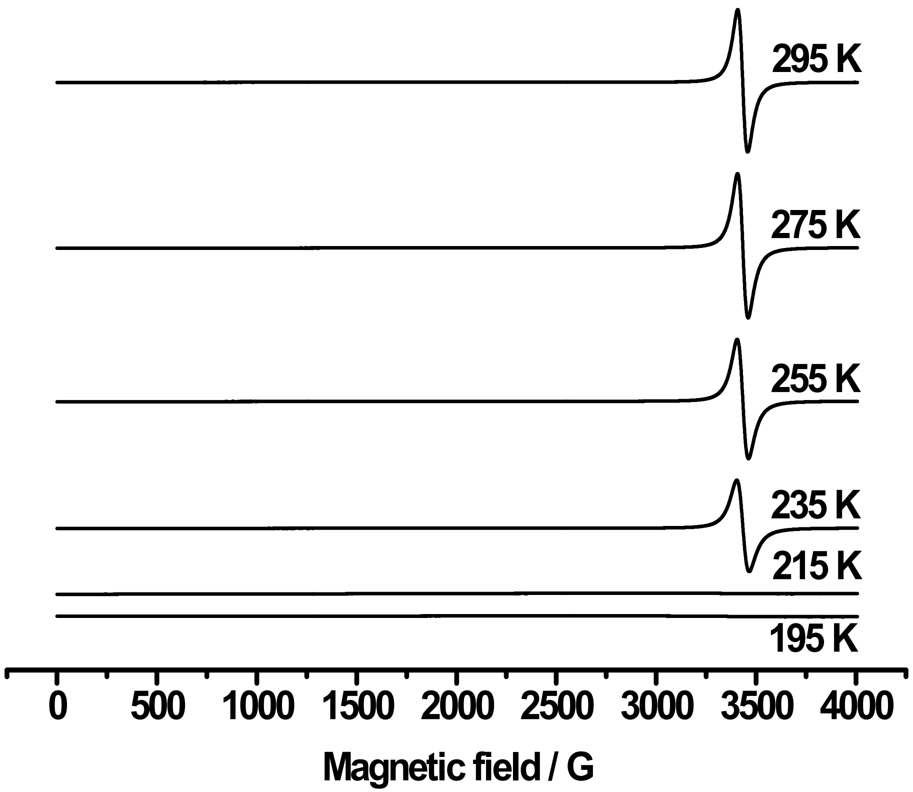


Figure 11S. Temperature dependence of the ESR spectrum of the [(bpy)FeCl$_3$] complex in acetonitrile (g = 2.012, $\Delta H_{pk\text{-}pk}$ = 50 G at room temperature)

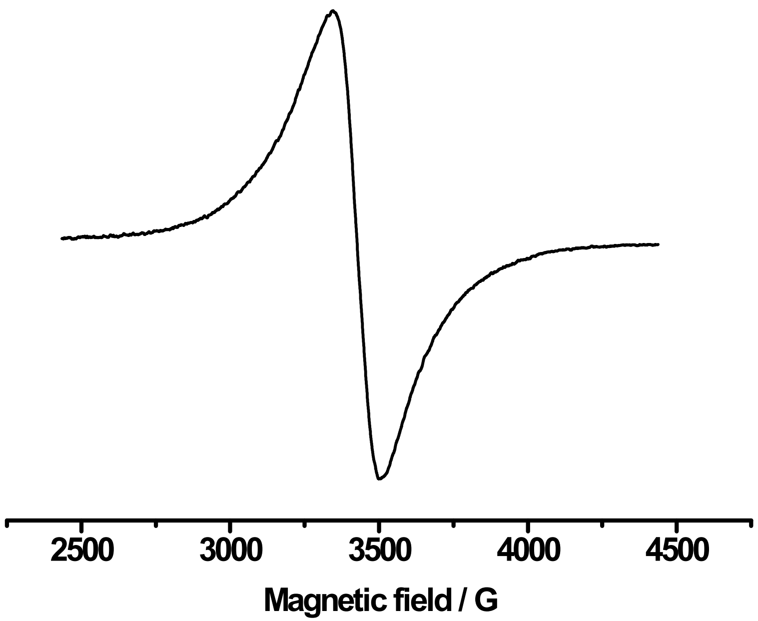


Figure 12S. ESR spectrum of the [(bpy)FeCl$_3$] complex solution at room temperature in CH$_2$Cl$_2$ (g = 2.014, $\Delta H_{\text{pk-pk}}$ = 150 G)

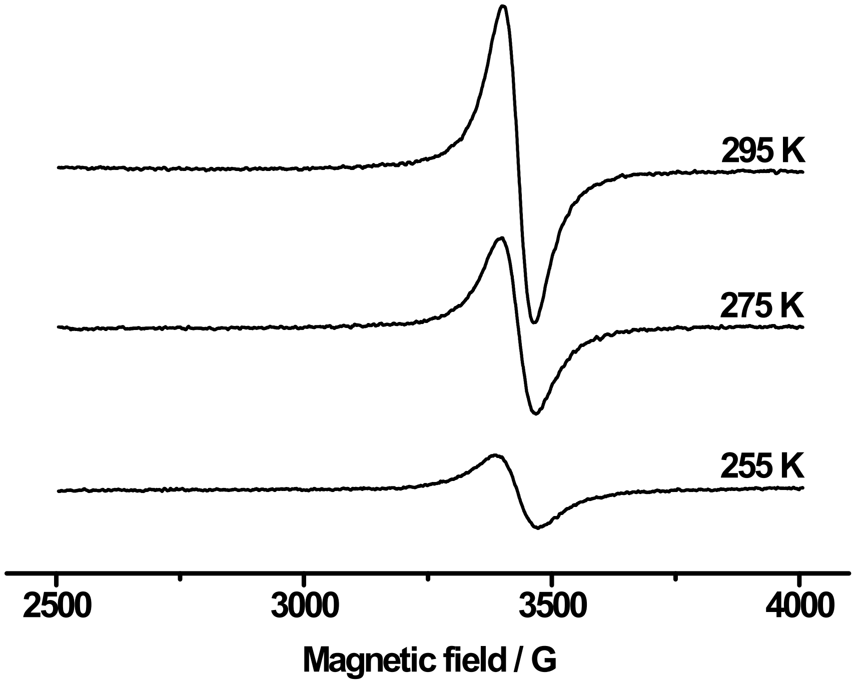


Figure 13S. Temperature dependence of the ESR spectrum of the mixture of [(bpy)$FeCl_2$] complex and R_FI in the 1: 1 ratio in DMF (g = 2.014, ΔH_{pk-pk} = 60 G at room temperature)

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