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From molecular wires to potential molecular cables

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ABSTRACT

Triple-helices with additional functional groups for anchoring on metal electrodes are accessible via metal-coordination assisted self-assembling.

With the development of new techniques for the investigation of molecules contacted to surfaces, and for instance to electrodes, electronic properties of numerous chemical structures have been studied [1]. However, only a few hundreds of so called molecular wires have been chemically contacted between two electrodes [2]. The investigation and understanding of the influence of the chemical structure and the molecule-electrode contact on the current-transport characteristics is essential for the potential use of molecules in future commercial electronic devices.

The use of metal-complexes integrated in nanosystems is particularly promising for applications like information storage. Among plenty of coordination compounds, polymetallic helical structures show adequate structural features for contacting both sides to metal electrodes [3]. However, to our knowledge, triple helicates functionalized with anchoring groups for metal surface decoration have never been reported. This is even more surprising since several examples of double or triple bimetallic helicates have been reported in the literature [4]. Among them, the 4,4'-methylenedianiline bridging motif combines the simplicity of the synthesis and structural modification [5]. In addition, various metals have already been complexed with derivatives of this molecule, and recently an enantiomeric resolution has even been reported with analogous compounds [6].

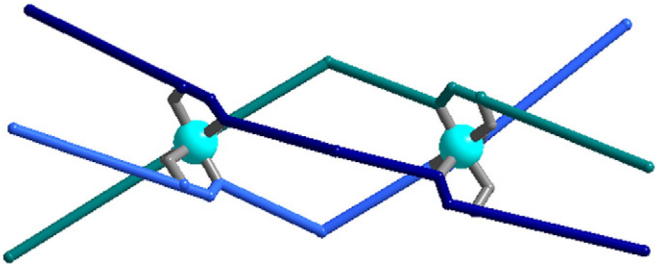
In the course for the development of new electronic-active molecular scaffolds, we designed and synthesized bimetallic helical complexes based on a 4,4'-methylenedianiline bridging motif (Scheme 1). More than a combination of three molecular organic wires with new structural features, this work highlights the potential possibility to tune the electronic transport properties by varying the metal ions. In view of the recent studies concerning metal complexes connected between electrodes, such potential molecular cables are of highest interest in the field of molecular electronics [7].

In this communication, we present the synthesis of two triple helices made by the assembling of three organic ligands L^1 around two zinc(II) or iron(II) cations respectively. This preliminary work emphasises the simplicity of the strategy to build hybrid scaffolds combining rigidity and functionality of the organic structure, and additional properties of metal complexes.

The ligand L^1 was synthesized in three steps (Scheme 2). First, a 5-bromo-pyridine-2-carboxaldehyde was prepared following a reported procedure [8]. A Suzuki-type cross-coupling reaction with 4-thiomethyl-phenyl-boronic acid gave the thiomethyl-functionalized aldehyde in good yield. Finally, a double imine-condensation of this latter with 4,4'-methylenedianiline in ethanol afforded the desired ligand [9].

Both complexes were synthesized by mixing a CH_2Cl_2/MeOH 5/1 solution of the ligand L^1 with a MeOH solution of the corresponding metal salt. While the perchlorate salt of the $L^1{}_3Zn_2$ complex precipitated during the reaction, the hexafluorophosphate salt of the $L^1{}_3Fe_2$ complex could be obtained by addition of a methanolic NH_4PF_6 solution [10,11].

The two binuclear complexes were characterised by ^{1} H NMR, IR, UV–vis spectroscopy, ESI mass spectrometry, elemental analysis, and single-crystal X-ray diffraction.



Scheme 1. Double end-functionalized dinuclear triple helices.

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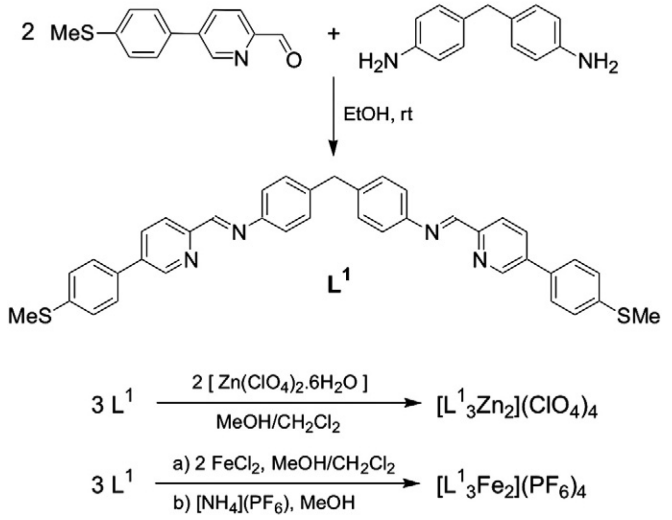

Scheme 2. Synthesis of the functionalized ligand L^1 and its two binuclear metal complexes.

Interestingly, while the zinc(II) helix shows a clearly resolved ^1H NMR spectrum, the iron(II) helix shows two broad bands at 5.68 and 7.00 ppm (Fig. 1). This can be ascribed to the hindered phenyl ring rotation between the two metals, as suggested for a similar compound [12]. Temperature dependent ^1H NMR spectra support this conclusion.

Another different behaviour between the two helical structures in solution is observed in the ESI mass spectra. While the perchlorate salt yields predominantly the $[L^1{}_3Zn_2]^{4+}$ ($=[M]^{4+}$) and the $[M+ClO_4]^{3+}$ peaks (Fig. 2), the mass spectrum of the hexafluorophosphate salt displays additional peaks which can be attributed to aggregation of several helical complexes with its counterion of general form $[M_x(PF_6)_y]^{(4x-y)+}$. However, the cation/ligand ratio is always in agreement with a triple helical bimetallic structure, confirming its very selective formation.

Single crystals of the Zn_2-helix suitable for X-ray analysis were obtained from an acetonitrile solution. The compound crystallises in the monoclinic space group $C2/c$ with six acetonitrile solvate molecules per formula unit. As expected, three ligands fold around two metal ions in a helical shape (Fig. 3). The zinc cations are complexed by the pyridine-imine chelating groups, forcing a distorted octahedral geometry. As expected, the six sulphur atoms are located on both sides of the helical structures. The two planes containing respectively the three outer sulphur atoms are nearly coplanar (10.5°) rendering them almost ideal for contacting them between metal (gold) electrodes. The intermetallic distance in this complex is 1.187 nm.

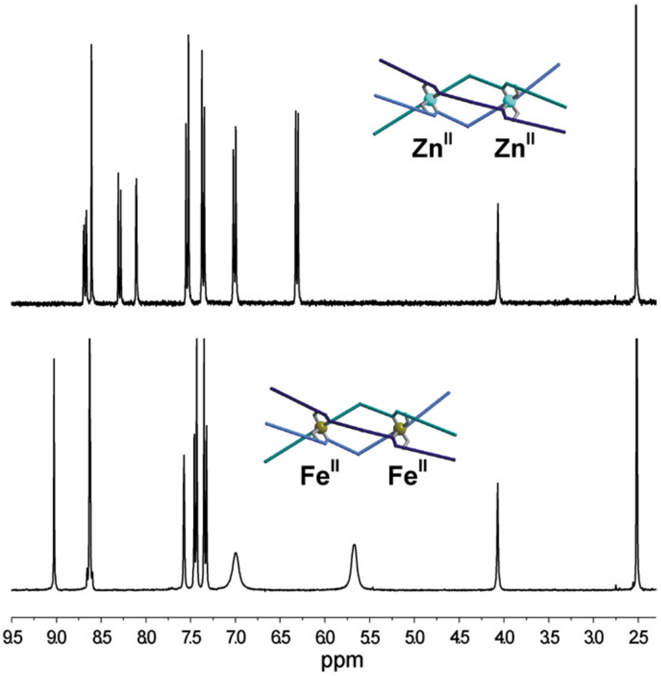

Fig. 1. ^1H NMR spectra of the two complexes at room temperature.

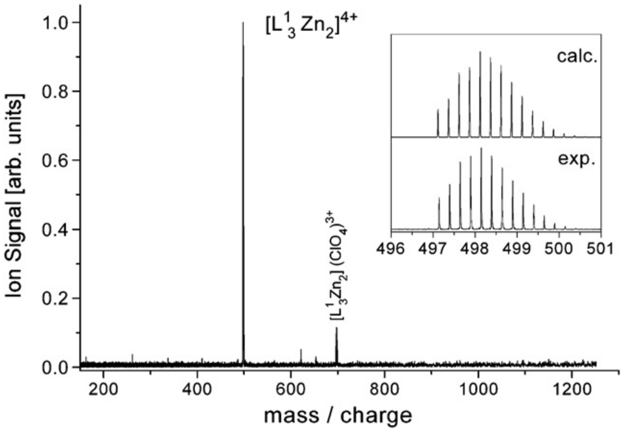

Fig. 2. ESI mass spectrum of the dinuclear zinc(II) helix in MeCN. (Inset: isotopic distribution of the $[L^1{}_3Zn_2]^{4+}$ complex, $L^1=C_{39}H_{32}N_4S_2$).

Single crystals of the Fe_2-complex suitable for X-ray analysis were obtained from a $MeCN/Et_2O$ solution [13]. In addition to the similar triple helical arrangement of the ligands around the two metal ions, this reveals the presence of four PF_6^- anions as expected for a bis-iron (II) complex in perfect agreement with the mass spectrometric finding of quadruply charged complex cation. The intermetallic distance in this second complex is 1.144 nm.

A careful look at the crystal structure shows the difference of distances between the bridging phenyl rings between both complexes (Fig. 4). The shorter distances of the carbon atoms connected to the imine nitrogen of the Fe(II) complex are induced by the shorter metal–nitrogen bond distances. This observation is in agreement with the hindered rotation of the phenyl rings in this compound as state above.

In the present communication, we report a new synthetic route of potential nano-cables suited for molecular electronics. Using this strategy, we succeeded in the preparation, and complete chemical and structural characterization of two new coordination compounds with additional groups for metal surface anchoring. Formed by the self-assembly of three conjugated organic rods around two metal ions, this work highlights the large variety of the possible structural modifications.

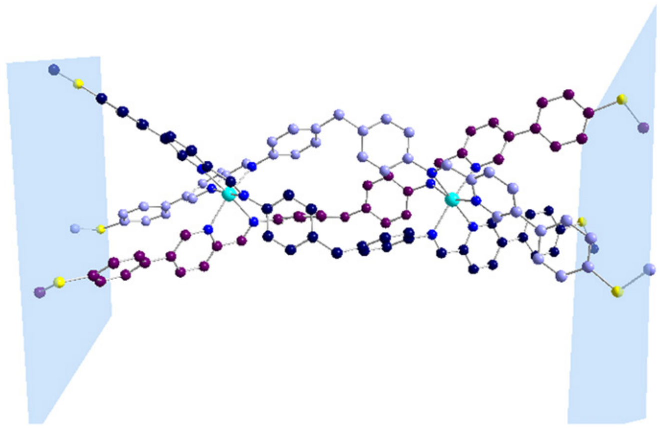

Fig. 3. View of the bis-zinc(II) triple helicate showing the internuclear distance. Perchlorate anions have been omitted for clarity.

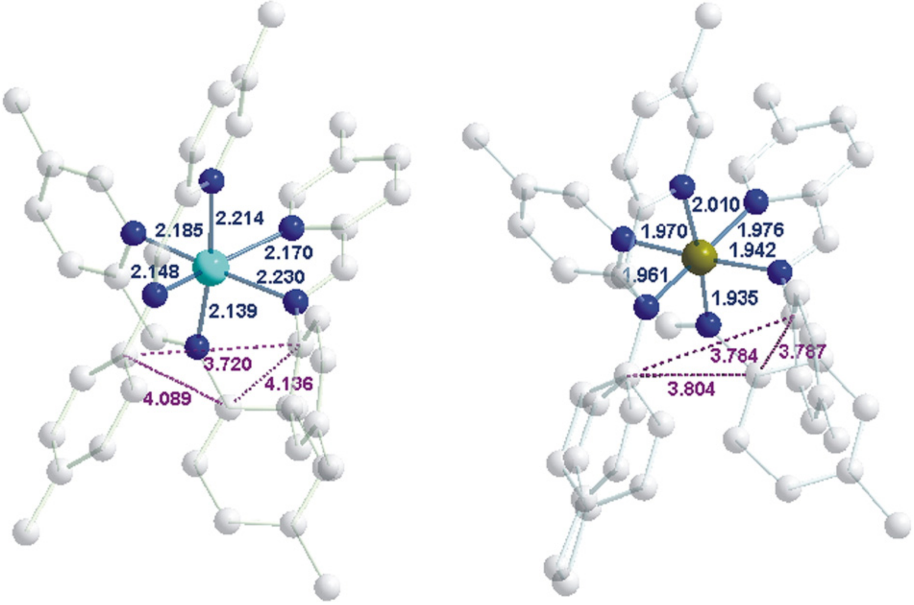

Fig. 4. View of the coordination sphere with the M–N distances (in blue), and the nearest C atoms of the phenyl rings (in purple) for the Zn(II) and the Fe(II) cations respectively.

The syntheses of derivatives with different bridging units, anchoring groups and metal ions appear very promising.

Acknowledgements

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Appendix A. Supplementary material

CCDC 667923 and 667924 contain the 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. Supplementary mzterial associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.09.026.

References[1]

[1] M.A. Ratner, Mater. Today (2002) 20;
C. Joachim, J.K. Gimzewski, A. Aviram, Nature 408 (2000) 541;
M. Mayor, H.B. Weber, Chimia 56 (2003) 494;
J.R. Heath, M.A. Ratner, Phys. Today 56 (2003) 43.

[2] F. Rosei, M. Schunack, Y. Naitoh, P. Jiang, A. Gourdon, E. Leagsgaard, I. Stengaard, C. Joachim, F. Besenbacher, Prog. Surf. Sci. 71 (2003) 95;
N.S. Hush, Ann. N.Y. Acad. Sci. 1006 (2003) 1;
J.R. Heath, M.A. Ratner, Phys. Today (2003) 43;
C. Joachim, M.A. Ratner, PNAS 102 (2005) 8801.

[3] S.-Y. Lin, I.-W.P. Chen, C. Chen, M.-H. Hsieh, C.-Y. Yeh, T.-W. Lin, Y.-H. Chen, S.-M. Peng, J. Phys. Chem. B 108 (2004) 959.

[4] L.J. Charbonnière, A.F. Williams, C. Piguet, G. Bernardinelli, E. Rivara-Minten, Chem. Eur. J. 4 (1998) 485;
M.J. Hannon, C.L. Painting, N.W. Alcock, Chem. Commun. (1999) 2023;
N. Yoshida, K. Ichikawa, M. Shiro, Perkin Trans. 2 (2000) 17;
G. Dong, P. Ke-liang, D. Chun-ying, H. Cheng, M. Qing-jin, Inorg. Chem. 41 (2002) 5978;
E.C. Constable, I.A. Hougen, C.E. Hausecroft, M. Neuburger, S. Schaffner, L.A. Whall, Inorg. Chem. Commun. 7 (2004) 1128;
S. Goetz, P.E. Kruger, Dalton Trans. (2006) 1277.

[5] N. Yoshida, K. Ichikawa, Chem. Commun. (1997) 1091;
M.J. Hannon, C.L. Painting, A. Jackson, J. Hamblin, W. Errington, Chem. Commun. 1807 (1997).

[6] J.M.C.A. Kerckhoffs, J.C. Peberdy, I. Meistermann, L.J. Childs, C.J. Isaac, C.R. Pearmund, V. Reudegger, S. Khalid, N.W. Alcock, M.J. Hannon, A. Rodger, Dalton Trans. (2007) 734.

[7] J. Park, A.N. Pasupathy, J.I. Goldsmith, C. Chang, Y. Yaish, J.R. Petta, M. Rinkoski, J.P. Sethna, H.D. Abruña, P.L. McEuen, D.C. Ralph, Nature 417 (2002) 722;
W. Han, E.N. Durantini, T.A. Moore, A.L. Moore, D. Gust, P. Rez, G. Leatherman, G.R. Seely, N. Tao, S.M. Lindsay, J. Phys. Chem. B 101 (1997) 10719;
V. Arima, E. Fabiano, R.I.R. Blyth, F.D. Sala, F. Matino, J. Thompson, R. Cingolani, R. Rinaldi, J. Am. Chem. Soc. 126 (2004) 16951;
T. Albrecht, A. Guckian, J. Ulstrup, J.G. Vos, Nano Lett. 5 (2005) 1451.

[8] J.J. Song, N.K. Yee, Z. Tan, J. Xu, S.R. Kapadia, C.H. Senanayake, Org. Lett. 6 (2004) 4905.

[9] *Synthesis of ligand **L**^{1}:* 4,4'–methylenedianiline (1.23 mmol) and 4-(4'-methylthio)-phenyl-salicylaldehyde (2.47 mmol) were mixed in EtOH (40 mL) and stirred at rt for 3 h. The yellow precipitate obtained was filtered, washed with EtOH (2x2 mL) and recrystallized from EtOH/CH_2Cl_2 to give the ligand as a yellowish solid in 91% yield. Calc. for $C_{39}H_{32}N_4S_2$ (Mr = 620.83): C: 75.45, H: 5.20, N: 9.02, S: 10.33, found: C: 75.25, H: 5.17, N: 9.07, S: 10.34; ^{1}H NMR ($C_2D_2Cl_2$): δ (ppm) 2.46 (s, 6H), 3.98 (s, 2H), 7.21 (s, 8H), 7.29 (d, $J = 8.3$ Hz, 4H), 7.51 (d, $J = 8.3$ Hz, 4H), 7.92 (dd, $J_1 = 8.3$ Hz, $J_2 = 2.2$ Hz, 2H), 8.19 (d, $J = 8.2$ Hz, 2H), 8.59 (s, 2H), 8.83 (d, $J = 2.2$ Hz, 2H); MALDI-TOF (no matrix), *m/z* (%): 621.0 (100) $[M+H]^+$; IR selected (KBr pellet): $\tilde{\upsilon}$ (cm–1) 1625, 1594, 1582, 1500, 1472, 1097, 998, 817, 529; UV-vis (MeCN) λ, nm (ε, $M^{-1}cm^{-1}$): 346 (100800), 232 (54400).

[10] *Synthesis of **Zn_2-Helix:*** $Zn(ClO_4)_2 \cdot 6H_2O$ (59.8 µmol) in MeOH (5 mL) was added to a solution of the ligand L^1 (89.8 µmol) in CH_2Cl_2/MeOH 5/1 (30 mL). After stirring overnight, the precipitate was filtered and washed with MeOH to yield the desired Zn_2-helical complex in 70% yield. Calc. for $[C_{117}H_{96}N_{12}S_6Zn_2](ClO_4)_4 \cdot 2H_2O$ C: 57.90, H:4.15, N:6.93, found: C:57.96, H:4.30, N:6.95; ^{1}H NMR (CD_3CN): δ (ppm) 2.52 (s, 18H), 4.07 (s, 6H), 6.32 (d, $J = 8.4$ Hz, 12H), 7.02 (d, $J = 8.3$ Hz, 12H), 7.36 (d, $J = 8.6$ Hz, 12H), 7.54 (d, $J = 8.6$ Hz, 12H), 8.11 (d, $J = 2.1$ Hz, 6H), 8.30 (d, $J = 8.1$ Hz, 6H), 8.61 (s, 6H), 8.68 (dd, $^3J = 8.2$, $^4J = 2.2$ Hz, 6H); ESI (MeCN): positive mode *m/z* (%) 498.1 (100) $[Zn_2L_3]^{4+}$; negative mode *m/z* (%): 98.8 (100) $[ClO_4]^{1-}$; IR selected (KBr pellet,): $\tilde{\upsilon}$ (cm–1) 1629, 1593, 1567, 1501, 1479, 1197, 1098, 1003, 818, 623; UV-vis (MeCN) λ, nm (ε, $M^{-1}cm^{-1}$): 379 (138500), 272 (104300).

[11] *Synthesis of **Fe_2-Helix:*** To a solution of L^1 (16.1 µmol) in CH_2Cl_2/MeOH, 5/1 (60 mL) was added $FeCl_2 \cdot 4H_2O$ (12.0 µmol) in MeOH (10 mL). After stirring at r.t. for 3 h, the resulting solution was filtered. Addition of NH_4PF_6 (1.07 mmol) in MeOH (10

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[1] Perchlorate salts should be handled carefully, in low quantities, used as hydrated salts, and never dehydrated under vacuum before used. Mass spectrometry: Electrospray ionisation (ESI) mass spectra were taken on a 7T-Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer (APEX II, Bruker Daltonik) from solutions of the Fe_2- and the Zn_2-Helix in acetonitrile. *Crystal data and structure refinement:* Data were collected at 180(2) K on a STOE IPDS II diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å). *Zn_2-Helix:* The structure was solved by direct methods and refined by full-matrix least-squares analysis. $[C_{117}H_{96}N_{12}S_6Zn_2](ClO_4)_4 \cdot 6(C_2H_3N)$, M = 2637.38, monoclinic, a = 51.717 (10), b = 10.223(2), c = 25.735(5) Å, β = 114.10(3)°, V = 12420(4) Å^3, space group C2/c, Z = 4, μ(MoKα) = 0.464 mm^{-1}, 22463 reflections measured, 9446 unique [R(int) = 0.1186]. $R_1 = 0.0768$ (for [I > 2σ(I)]), wR2 = 0.1436 (for all data). CCDC 667923. *Fe_2-Helix:*[13] $[C_{117}H_{96}Fe_2N_{12}S_6](PF_6)_4 \cdot 8(C_2H_3N)$, M = 2877.39, monoclinic, a = 30.542(6), b = 20.286(4), c = 11.599(2) Å, β = 94.39(3)°, V = 7165(2) Å^3, space group *C*2, Z = 2, *μ*(MoKα) = 0.420 mm^{-1}, 18783 reflections measured, 7962 unique [R(int) = 0.0650]. $R_1 = 0.1003$ (for [I > 2σ(I)]), wR2 = 0.2473 (for all data) FLACK parameter 0.44(4). CCDC 667924.

mL) gave a dark violet precipitate. After overnight stirring, the solid was collected and washed with MeOH to yield the Fe2-helical complex in 46% yield. Calc. for $[C_{117}H_{96}Fe_2N_{12}S_6](PF_6)_4 \cdot 2H_2O$, C:54.26, H:3.89, N:6.49, found: C:54.23, H:3.97, N: 6.47; Calc. for $[C_{117}H_{96}N_{12}S_6Fe_2](PF_6)_4$ ($M_r = 2554.03$): C, 55.02, H, 3.79, N, 6.58; S, 7.53, found (dried at 110°C, 10–3 mbar): C, 54.85, H, 3.96, N, 6.60, S, 7.68; ^{1}H NMR (CD_3CN, 25°C): δ (ppm) 2.52 (s, 18H), 4.08 (s, 6H), 5.68 (br s, 12H), 7.00 (br s, 12H), 7.33 (d, $J = 8.7$ Hz, 12H), 7.44 (d, $J = 8.7$ Hz, 12H), 7.61 (s, 6H), 8.60-8.67 (m, 12H), 9.07 (s, 6H); ESI (MeCN): positive mode *m/z* (%) 493.4 (100) $[Fe_2L_3]^{4+}$, 664.2 (31) $[Fe_2L_3F]^{3+}$, 1068.8 (5) $[Fe_2L_3(PF_6)F]^{2+}$, 1132.0 (24) $[2(Fe_2L_3)_24(PF_6)]^{4+}$, 1387.3 (19) $[3(Fe_2L_3)7(PF_6)]^{5+}$, 1557.4 (11) $[2(Fe_2L_3)5(PF_6)]^{3+}$, 1770.2 (14) $[3(Fe_2L_3)8(PF_6)]^{4+}$, 1898.3 (9) $[4(Fe_2L_3)11(PF_6)]^{5+}$, 2409 (15) $[Fe_2L_3(PF_6)_3]^{1+}$; negative mode *m/z* (%) = 144.7 (100) $[PF_6]^{1-}$; IR selected (KBr pellet): $\tilde{\upsilon}$ (cm^{-1}) 3439, 1589, 1558, 1541, 1499, 1473, 1199, 1097, 842, 556; UV-VIS (MeCN) λ, nm (ε, M–1cm–1): 589 (16800), 372 (119800), 272 (119900).

[12] M. Pascu, G.J. Clarkson, B.M. Kariuki, M.J. Hannon, Dalton Trans. (2006) 2635.

[13] The quality of the crystals of the Fe complex was very poor with only diffuse diffraction for angles $2\theta > 48°$. The FLACK parameter indicates that the measured crystal was a racemic twin. Some phenyl rings and the couterions (PF_6–) were refined disordered. Also the solvent molecules were difficult to localise because of disorder.