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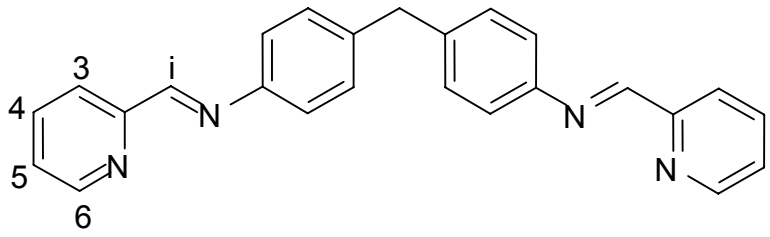
Supplementary Information

Characterisation Data

NMR spectra were recorded on a Bruker DPX 300/400 MHz instrument using standard Bruker software. Electrospray Ionisation (ESI) analyses were performed by the EPSRC National Mass Spectrometry Service Centre, Swansea, on a Micromass Quatro (II) instrument in positive ionisation mode. Microanalyses were conducted on a Leeman Labs CE44 CHN analyser by Warwick Analytical Service Ltd. Infrared spectra were recorded with a Perkin Elmer Paragon 1000 FTIR spectrometer.



Complex 1 ($[Fe_2(C_{25}H_{20}N_4)_3][PF_6]_4$).

Found C, 47.3; H, 3.3; N, 8.7. Calc. for $[Fe_2(C_{25}H_{20}N_4)_3][(PF_6)_4]\bullet 4.0\ H_2O$: C, 47.6; H, 3.6; H, 8.9%. $\upsilon_{max/cm^{-1}}$ (selected data, $[Fe_2(C_{25}H_{20}N_4)_3][PF_6]_4$) 1615m, 1585m, 1558w, 1502s, 1473m, 1440m, 1414w, 1302s, 1256w, 1239m, 1206s, 1162m, 1111m, 1018s, 832vs cm^{-1}. δ_H (400 MHz, CD_3CN, $[Fe_2(C_{25}H_{20}N_4)_3][PF_6]_4$) 3.98 (2H, s, CH_2), 5.17 (2H, d, J = 7.4 Hz, H_{Ph}), 5.75 (2H, d, J = 6.9 Hz, H_{Ph}), 6.55 (2H, d, J = 7.8 Hz, H_{Ph}), 7.22 (4H, m, H_6,H_{Ph}), 7.68 (2H, t, J = 6.4 Hz, H_5), 8.34 (2H, t, J = 7.4 Hz, H_4), 8.48 (2H, d, J = 7.4 Hz, H_3), 8.75 (2H, s, H_i). Positive-ion ESI (MeCN, $[Fe_2(C_{25}H_{20}N_4)_3][PF_6]_4$): *m/z* 462 ($[Fe_2(L^1)_3(PF_6)]^{3+}$, 421 ($[Fe_2(L^1)_3(F)]^{3+}$, 331.0 ($[Fe_2(L^1)_3]^{4+}$. UV/Vis (MeCN, $[Fe_2(C_{25}H_{20}N_4)_3][PF_6]_4$): 524 ($\varepsilon = 11{,}500$), 572 ($\varepsilon = 15{,}300$) nm.

Complex 2 ($[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$) / ($[Fe_2(C_{27}H_{24}N_4)_3][Cl]_4$).

Found C, 56.6; H, 4.3; N, 9.7. Calc. for ($[Fe_2(C_{27}H_{24}N_4)_3][Cl_4]\bullet 2.5(CHCl_3)$): C, 56.8; H, 4.3; H, 9.5%. $\upsilon_{max/cm^{-1}}$ (selected data, $[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$) 3386w, 1626w, 1588w, 1559w, 1503m, 1474m, 1441m, 1380m, 1334m, 1308w, 1256m, 1166w, 1110w, 1060w, 1019w, 828vs, 771vs, 750vs, 691m, 674m. δ_H (400 MHz, MeOD-*d4*, $[Fe_2(C_{25}H_{20}N_4)_3][Cl]_4$) 4.10 (3H, s, Me), 4.64 (3H, s, Me), 4.79 (2 H, dd, J = 8.3 Hz, J = 1.5 Hz, H_{Ph}), 5.57 (2H, dd, J = 8.3 Hz, J = 1.5 Hz, CH_{Ph}), 6.89 (2H, dd, J = 6.3

Hz, CH_{Ph}), 7.26 (2H, d, J = 6.3 Hz, $H_{3/6}$), 7.42 (2H, dd, J = 6.3 Hz, J = 1.1 Hz, H_{Ph}), 7.81 (2H, t, J = 6.3 Hz, $H_{4/5}$), 8.50 (2H, t, J = 7.8 Hz, $H_{4/5}$), 8.78 (2H, d, J = 7.8 Hz, $H_{3/6}$). Positive-ion ESI ($[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$): *m/z* 331.4 ($[Fe_2(L^2)_3]^{4+}$).

Complex 3 ($[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$).

Found C, 50.8; H, 4.1; N, 8.8. Calc. for ($[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$): C, 51.1; H, 3.8; H, 8.8%. $\upsilon_{max/cm^{-1}}$ (selected data, ($[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$) 3386w, 1626w, 1588w, 1558w, 1503w, 1474m, 1441m, 1380m, 1335m, 1308w, 1256w, 1166w, 1110w, 1060w, 1019w, 828vs, 771vs, 750vs, 691m, 674m. δ_H (300 MHz, CD_3CN, ($[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$) 2.85 (6 H, s, Me), 4.02 (2 H, s, CH_2), 5.28 (2H, br s, H_{Ph}), 5.74 (2H, br s, H_{Ph}), 6.63 (2H, br s, H_{Ph}), 7.07 (2H, d, J = 4.5 Hz, $H_{4/6}$), 7.31 (2H, br s, H_{Ph}), 7.61 (2H, br t, H_5), 8.15 (2H, d, J = 7.0 Hz, $H_{4/6}$), 8.97 (2H, s, H_i). Positive-ion ESI (MeCN, ($[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$): *m/z* 1760.1 ($[Fe_2(L^3)_3(PF_6)_3]^+$), 807.2 ($[Fe_2(L^3)_3(PF_6)_2]^{2+}$), 489.9 ($[Fe_2(L^3)_3(PF_6)]^{3+}$), 331.2 ($[Fe_2(L^3)_3]^{4+}$).

Complex 4 ($[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$).

δ_H (300 MHz, CD_3CN, $[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$) 2.72 (6 H, s, Me), 4.03 (2 H, s, CH_2), 5.53 (4H, br s, H_{Ph}), 6.97 (4H, br s, H_{Ph}), 7.17 (2H, s, ArH), 7.61 (2H, s, ArH), 8.38 (2H, s, ArH), 8.87 (2H, s, H_i).

Complex 5 ($[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$) / ($[Fe_2(C_{27}H_{24}N_4)_3][Cl]_4$)

Found C, 50.8; H, 4.0; N, 8.6. Calc. for ($[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$): C, 51.1; H, 3.8; H, 8.8%.. $\upsilon_{max/cm^{-1}}$ (selected data, ($[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$) 3137w, 2350w, 1625m, 1597w, 1561w, 1499s, 1354w, 1221m, 1197s, 1106w, 1040m, 1016w, 912s, 836s, 770m, 748w, 658w. δ_H (400 MHz, MeOD-*d4*, ($[Fe_2(C_{27}H_{24}N_4)_3][Cl]_4$) 2.48 (6H, s, Me), 4.08 (2H, s, Me), 5.59 (4H, br s, H_{Ph}), 7.04 (4H, br s, H_{Ph}), 7.31 (2H, s, H_5), 8.33 (2H, d, J = 7.5 Hz, $H_{3/4}$), 8.62 (2H, d, J = 8.0 Hz, $H_{3/4}$), 9.16 (2H, s, H_i). Positive-ion ESI (MeCN, ($[Fe_2(C_{27}H_{24}N_4)_3][PF_6]_4$): *m/z* 1761.1 ($[Fe_2(L^5)_3(PF_6)_3]^+$), 807.4 ($[Fe_2(L^5)_3(PF_6)_2]^{2+}$), 490.2 ($[Fe_2(L^5)_3(PF_6)]^{3+}$), 331.4 ($[Fe_2(L^5)_3]^{4+}$).

Complex 6 ($[Fe_2(C_{29}H_{28}N_4)_3][PF_6]_4$ / ($[Fe_2(C_{29}H_{28}N_4)_3][Cl]_4$).

Found C, 52.0; H, 4.2; N, 8.3. Calc. for ($[Fe_2(C_{29}H_{28}N_4)_3][PF_6]_4 \bullet (H_2O)$): C, 52.1; H, 4.3; N, 8.4%. $\upsilon_{max/cm^{-1}}$ (selected data, ($[Fe_2(C_{29}H_{28}N_4)_3][Cl]_4$) 3386w, 1613w, 1590w,

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1503s, 1475m, 1441m, 1379m, 1335m, 1310w, 1221w, 1166w, 1110w, 1042w, 1018w, 828vs, 773vs, 750vs, 691m, 674m. δ_H (300 MHz, CD_3CN, ($[Fe_2(C_{29}H_{28}N_4)_3][PF_6]_4$) 2.35 (6H, s, Me), 2.71 (6H, s, Me), 4.01 (2H, s, CH_2), 4.67 (2H, dd, J = 8.3 Hz, J = 1.9 Hz, H_{Ph}), 5.47 (2H, dd, J = 8.0 Hz, J = 2.0 Hz, H_{Ph}), 6.76 (2H, d, J = 8.1 Hz, H_{Ph},), 6.93 (2H, d, J = 5.6 Hz, $H_{5/6}$), 7.31 (2H, d, J = 7.6 Hz, H_{Ph}), 7.51 (2H, d, J = 5.3 Hz, $H_{5/6}$), 8.45 (2H, s, H_3). Positive-ion ESI (MeOH, $[Fe_2(C_{29}H_{28}N_4)_3][Cl]_4$): *m/z* 352.4 ($[Fe_2(L^6)_3]^{4+}$). Positive-ion ESI (MeCN, $[Fe_2(C_{29}H_{28}N_4)_3][PF_6]_4$): *m/z* 1844.6 ($[Fe_2(L^6)_3(PF_6)_3]^+$), 850.0 ($[Fe_2(L^6)_3(PF_6)_2]^{2+}$, 518.2 ($[Fe_2(L^6)_3(PF_6)]^{3+}$), 352.4 ($[Fe_2(L^6)_3]^{4+}$).

Complex 7 ($[Fe_2(C_{24}H_{18}N_4O)_3][PF_6]_4$ / $[Fe_2(C_{24}H_{18}N_4O)_3][Cl]_4$.

Found C, 59.8; H, 4.3; N, 11.6. Calc. for ($[Fe_2(C_{24}H_{18}N_4O)_3][Cl]_4$•3.0($H_2O$)): C, 59.9; H, 4.2; H, 11.7%. $\upsilon_{max/cm^{-1}}$ (selected data, ($[Fe_2(C_{24}H_{18}N_4O)_3][PF_6]_4$) 1626w, 1591w, 1488vs, 1441w, 1357w, 1227s, 1195s, 1158m, 1105w, 1043w, 1011w, 834vs, 774vs. δ_H (300 MHz, D_2O, $[Fe_2(C_{24}H_{18}N_4O)_3][Cl]_4$): 5.35 (2H, br s, H_{Ph}), 5.88 (2H, br s, H_{Ph}), 6.39 (2H, br s, H_{Ph}), 7.03 (2H, br s, H_{Ph}), 7.26 (2H, d, J = 4.7 Hz, $H_{3/6}$), 7.57 (2H, t, J = 4.8 Hz, $H_{4/5}$), 8.23 (2H, t, J = 7.4 Hz, $H_{4/5}$), 8.43 (2H, d, J = 7.5 Hz, $H_{3/6}$), 8.99 (2H, s, H_i). Positive-ion ESI (MeCN, $[Fe_2(C_{24}H_{18}N_4O)_3][PF_6]_4$): *m/z* 1681 ($[Fe_2(L^7)_3(PF_4)_3]^+$), 768 ($[Fe_2(L^7)_3(PF_4)_2]^{2+}$, 464 ($[Fe_2(L^7)_3(PF_6)]^{3+}$), 312 ($[Fe_2(L^6)_3]^{4+}$). UV/Vis (MeCN, $[Fe_2(C_{24}H_{18}N_4O)_3][PF_6]_4$): 286 ($\varepsilon$ = 65,000), 329 (ε = 41,000), 522 (ε = 10,000), 571 (ε = 13,200) nm.

Complex 8 ($[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$.

Found C, 44.4; H, 3.4; N, 7.7. Calc. for ($[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$•2.0($CHCl_3$)): C, 44.7; H, 3.2; H, 7.8%. $\upsilon_{max/cm^{-1}}$ (selected data, ($[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$) 3381w, 1626w, 1588w, 1558w, 1503s, 1474m, 1441m, 1380m, 1335m, 1308w, 1256m, 1166w, 1110w, 1060w, 1019w, 827vs, 771vs, 750vs, 691m, 674m. δ_H (300 MHz, CD_3CN, $[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$) 2.44 (6H, s, Me), 4.88 (2H, d, J = 8.9 Hz, H_{Ph}), 5.62 (2H, d, J = 7.5 Hz, H_{Ph}), 6.57 (2H, d, J = 7.1 Hz, H_{Ph}), 7.10 (2H, d, J = 5.1 Hz, $H_{3/6}$), 7.24 (2H, d, J = 8.1 Hz, H_{Ph}), 7.69 (2H, t, J = 6.0 Hz, $H_{4/5}$), 8.38 (2H, t, J = 7.4 Hz, $H_{4/5}$), 8.62 (2H, d, J = 7.7 Hz, $H_{3/6}$). Positive-ion ESI (acetone / MeOH, $[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$): *m/z* 810.2 ($[Fe_2(L^8)_3(PF_6)_2]^{2+}$), 492.0 ($[Fe_2(L^8)_3(PF_6)]^{3+}$), 332.8 ($[Fe_2(L^8)_3]^{4+}$).

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Complex 9 ($[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$ / $([Fe_2(C_{26}H_{22}N_4O)_3][Cl]_4$.

Found C, 52.9; H, 4.7; N, 8.5. Calc. for ($[Fe_2(C_{26}H_{22}N_4O)_3][Cl]_4$•4.8($CH_2Cl_2$)): C, 52.9; H, 4.1; N, 8.9. $\upsilon_{max/cm^{-1}}$ (selected data, ($[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$) 3356w, 1614w, 1590w, 1490vs, 1446w, 1378w, 1311w, 1231s, 1164m, 1108w, 1038w, 1010w, 833vs, 792s, 691w, 674m. δ_H (400 MHz, CD_3CN, $[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$) 2.87 (6H, s, Me), 5.49 (2H, br s, H_{Ph}), 5.94 (2H, br s, H_{Ph}), 6.44 (2H, br s, H_{Ph}), 7.04 (2H, d, J = 6.1 Hz, $H_{4/6}$), 7.22 (2H, br s, H_{Ph}), 7.60 (2H, t, J = 7.2 Hz, H_5), 8.15 (2H, d, J = 7.0 Hz, $H_{4/6}$), 9.04 (2H, s, H_i). Positive-ion ESI (MeOH, $[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$): *m/z* 1765.3 ($[Fe_2(L^9)_3(PF_6)_3]^+$), 810.2 ($[Fe_2(L^9)_3(PF_6)_2]^{2+}$), 491.9 ($[Fe_2(L^9)_3(PF_6)]^{3+}$), 332.6 ($[Fe_2(L^9)_3]^{4+}$).

Complex 10. $[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$.

Found C, 49.5; H, 4.1; N, 8.3. Calc. for ($[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$•3.0(EtOH)): C, 49.2; H, 4.1; N, 8.2%. $\upsilon_{max/cm^{-1}}$ (selected data, ($[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$) 3386w, 1589w, 1562w, 1503m, 1474m, 1441m, 1380m, 1335m, 1308w, 1256m, 1166w, 1110w, 1060w, 1019w, 828vs, 771vs, 750vs, 691m, 674m. δ_H (400 MHz, CD_3CN, $[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$) 2.70 (6H, s, Me), 5.70 (4H, br s, H_{Ph}), 6.70 (4H, br s, H_{Ph}), 7.44 (2H, s, H_3), 7.72 (2H, d, J = 5.9 Hz, $H_{5/6}$), 8.51 (2H, d, J = 7.8 Hz, $H_{5/6}$) 9.30 (2H, s, H_i). Positive-ion ESI (MeCN, $[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$): *m/z* 1768.5 ($[Fe_2(L^{10})_3(PF_6)_3]^+$), 810.6 ($[Fe_2(L^{10})_3(PF_6)_2]^{2+}$), 492.2 ($[Fe_2(L^{10})_3(PF_6)]^{3+}$), 332.9 ($[Fe_2(L^{10})_3]^{4+}$).

Complex 11 $[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$ / $[Fe_2(C_{26}H_{22}N_4O)_3][Cl]_4$.

Found C, 44.3; H, 3.7; N, 8.8. Calc. for ($[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$•8.4($H_2O$)): C, 45.5; H, 4.1; N, 8.2%. $\upsilon_{max/cm^{-1}}$ (selected data, ($[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$) 3386w, 1626w, 1589w, 1558w, 1503m, 1474m, 1441m, 1380m, 1335m, 1308w, 1256w, 1198w, 1166w, 1110w, 1060w, 1019w, 827vs, 771vs, 750s, 691m, 674m. δ_H (400 MHz, MeOD-*d4*, $[Fe_2(C_{26}H_{22}N_4O)_3][Cl]_4$) 2.48 (6H, s, Me), 5.77 (4H, br s, H_{Ph}), 6.78 (4H, br s, H_{Ph}), 7.60 (2H, s, H_6), 8.30 (2H, d, J = 8.0 Hz, $H_{3/4}$), 8.73 (2H, d, J = 8.0 Hz, $H_{3/4}$) 9.60 (2H, s, H_i). Positive-ion ESI (MeCN, $[Fe_2(C_{26}H_{22}N_4O)_3][PF_6]_4$): *m/z* 333.1 ($[Fe_2(L^{11})_3]^{4+}$).

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Complex 12 ($[Fe_2(C_{28}H_{26}N_4O)_3][PF_6]_4$) / ($[Fe_2(C_{28}H_{26}N_4O)_3][Cl]_4$).

Found C, 48.0; H, 3.9; N, 8.0. Calc. for ($[Fe_2(C_{28}H_{26}N_4O)_3][PF_6]_4$•1.0($CHCl_3$)): C, 48.3; H, 3.8; N, 8.0%. $\upsilon_{max/cm^{-1}}$ (selected data, $[Fe_2(C_{28}H_{26}N_4O)_3][Cl]_4$) 3356w, 1615m, 1591m, 1490vs, 1446m, 1378m, 1311w, 1233s, 1202s, 1164m, 1104m, 1034m, 1010m, 831s, 690m, 674m. δ_H (300 MHz, D_2O, $[Fe_2(C_{28}H_{26}N_4O)_3][Cl]_4$) 2.38 (6H, s, Me), 2.62 (6H, s, Me) 4.88 (2H, dd, J = 8.7 Hz, J = 2.4 Hz, H_{Ph}), 5.65 (1H, d, J = 8.7 Hz, J = 2.5 Hz, H_{Ph}), 6.55 (2H, dd, J = 8.9 Hz. J = 2.5 Hz, H_{Ph}), 6.91 (2H, d, J = 5.9 Hz, $H_{5/6}$), 7.14 (2H, dd, J = 8.5 Hz, J = 2.5 Hz, H_{Ph}), 7.41 (2H, d, J = 5.8 Hz, $H_{5/6}$), 8.44 (2H, s, H_3). Positive-ion ESI (MeCN, $[Fe_2(C_{28}H_{26}N_4O)_3][PF_6]_4$): *m/z* 1849.9 ($[Fe_2(L^{12})_3(PF_6)_3]^+$), 852.9 ($[Fe_2(L^{12})_3(PF_6)_2]^{2+}$), 520.1 ($[Fe_2(L^{12})_3(PF_6)]^{3+}$), 354.0 ($[Fe_2(L^{12})_3]^{4+}$). Positive-ion ESI (MeOH, $[Fe_2(C_{29}H_{28}N_4O)_3][Cl]_4$): *m/z* 483.5 ($[Fe_2(L^{12})_3(Cl)]^{3+}$), 353.9 ($[Fe_2(L^{12})_3]^{4+}$).

Electronic Supplementary Information for Dalton Transactions
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