

Supporting Information

Dipyridylketone Thiosemicarbazone Iron Chelators: Pre-Complexation and Transmetallation Effects on Anti-Cancer Activity

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Page S11: Fig. S2. Difference absorption spectra showing formation of [Fe^{III}(Dp44mT)₂]³⁺

Elemental Analyses and spectroscopic data

[Mn^{II}(Dp4mT)₂]·H₂O: Brown powder (yield 56%). Anal. Calcd for C₂₆H₂₆MnN₁₀OS₂: C, 50.8; H, 4.3; N, 22.8 found C, 51.0; H, 4.7; N, 22.0%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1589m, 1481m, 1428s, 1370s, 1323m, 1236m, 1156s, 969m, 742s, 616s.

[Co^{III}(Dp4mT)₂](ClO₄)·4H₂O: Brown powder (yield 67%). Anal. Calcd for C₂₆H₃₂ClCoN₁₀O₈S₂: C, 40.5; H, 4.2; N, 18.2 found C, 40.5; H, 3.53; N, 17.6%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1557m, 1509m, 1451s, 1393s, 1304s, 1167m, 1072s, 786m, 744m, 618s. ¹H NMR (DMSO-d₆): 8.85 (q, 1H, pyr), 8.33 (t, 1H, pyr), 8.10 (d, 3H, pyr), 7.76 (d, 1H, pyr), 3.12 (d, 3H, -CH₃). ¹³C NMR (DMSO-d₆): 23.2, 114.5, 121.1, 122.6, 123.3, 133.8, 134.2, 146.9, 147.3, 149.5, 151.5, 155, 163.4 ppm.

Ni^{II}(Dp4mT)₂: Dark brown powder (yield 75%). Anal. Calcd for C₂₆H₂₄N₁₀Ni S₂: C, 52.1; H, 4.0; N, 23.3 found C, 51.9; H, 4.01; N, 22.7%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 3321m, 1590m, 1508m, 1425s, 1372s, 1330s, 1243s, 1148s, 782m, 745s.

[Cu^{II}(Dp4mT)₂]·4.5H₂O: Brown powder (yield 45%). Anal. Calcd for C₂₆H₃₃CuN₁₀ O_{4.5}S₂: C, 45.5; H, 4.8; N, 20.4; found C, 44.5; H, 3.8; N, 19.7%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 3293m, 1524m, 1446s, 1390s, 1083s, 785m, 618s.

Zn^{II}(Dp4mT)₂: Yellow powder (yield 87%). Anal. Calcd for C₂₆H₂₄N₁₀S₂Zn: C, 51.5; H, 3.9; N, 23.1; found C, 51.2; H, 3.9; N, 22.9%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 3326m, 1589m, 1511m, 1429s, 1369s, 1329s, 1245s, 1148s, 970m, 818s, 748m, 744s. ¹H NMR (DMSO-d₆): 8.74(d, 1H, pyr); 8.55(s, 1H, pyr); 7.95-8.00(m, 3H, pyr); 7.72(t, 1H, pyr); 7.48(t, 2H, pyr); 3.45 (d, 3H, -CH₃). ¹³C NMR (DMSO-d₆): 22.6, 119.7, 120.1, 121.6, 122.3, 131.8, 132.2, 145.9, 146.3, 148.5, 148.5, 159, 160.4 ppm.

[Mn^{II}(Dp44mT)₂]: Brown powder (yield 55%). Anal. Calcd for C₂₈H₂₈MnN₁₀S₂: C, 53.9; H, 4.5; N, 22.4; found C, 54.1; H, 4.6; N, 22.4%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1584m, 1453m, 1355s, 1299s, 1230s, 1200m, 1118s, 970s, 913s, 790s, 743s, 652m, 626s.

[Co^{III}(Dp44mT)₂](ClO₄)·1.5H₂O: Dark brown powder (yield 62%). Anal. Calcd for C₂₈H₃₁ClCoO_{5.5}N₁₀S₂: C, 44.6; H, 4.1; N, 18.5; found C, 44.6; H, 4.0; N, 18.6%. IR $\bar{\nu}_{\text{max}}$ (cm⁻¹): 1553m, 1508m, 1460m, 1391s, 1316s, 1251s, 1151m, 1081s, 912s, 785m, 748m, 620s. ¹H NMR (DMSO-d₆) (400MHz): 8.86(q, 1H, pyr); 8.35(t, 1H, pyr); 8.15-7.98 (m, 4H, pyr); 7.78 (d, 1H, pyr); 7.52-7.65 (t, 2H, pyr); 3.18 (d, 6H, -CH₃). ¹³C NMR (DMSO-d₆) (400MHz): 39.9, 41.5, 125.0, 126.6, 126.7, 127.7, 136.8, 139.8, 148.4, 149.4, 151.5, 155, 163.4 ppm.

Ni^{II}(Dp44mT)₂: Brown powder (yield 56%). Anal. Calcd for C₂₈H₂₈N₁₀NiS₂: C, 53.6; H, 4.5; N, 22.3; found C, 53.8; H, 4.4; N, 22.3%. IR $\bar{\nu}_{\text{max}}$ (cm⁻¹): 1584m, 1493m, 1452m, 1433m, 1357s, 1299s, 1265m, 1231s, 1195s, 1121s, 971m, 911s, 820m, 787s, 740s, 628s.

Cu^{II}(Dp44mT)₂: Brown powder (yield 71%). Anal. Calcd for C₂₈H₂₈Cu N₁₀S₂: C, 53.1; H, 4.4; N, 22.1; found C, 52.7; H, 4.6; N, 21.5%. IR $\bar{\nu}_{\text{max}}$ (cm⁻¹): 1582m, 1493m, 1456m, 1354s, 1303s, 1232s, 1131s, 1048m, 971m, 915s, 787s, 742s, 618s.

Zn^{II}(Dp44mT)₂: Yellow powder (yield 85%). Anal. Calcd for C₂₈H₂₈N₁₀S₂Zn: C, 53.0; H, 4.4; N, 22.0; found C, 52.8; H, 4.4; N, 21.9%. IR $\bar{\nu}_{\text{max}}$ (cm⁻¹): 1583m, 1496m, 1456m, 1355s, 1300s, 1232s, 1200m, 1122s, 1050m, 971s, 914s, 790s, 741s, 652m, 628s. ¹H NMR (DMSO-d₆): 8.26 (d, 1H, pyr); 8.15(s, 1H, pyr); 7.43-7.78 (m, 3H, pyr); 7.22 (t, 1H, pyr); 7.12 (t, 2H, pyr); 2.78 (d, 3H, -CH₃). ¹³C NMR (DMSO-d₆): 22.6, 119.7, 120.1, 121.6, 123.3, 131.8, 133.2, 145.9, 146.3, 148.5, 155.5, 159, 164.4 ppm.

[Mn^{II}(Dp4aT)₂].1.5 H₂O: Brown powder (yield 66%). Anal. Calcd for C₃₀H₃₁N₁₀O_{1.5}S₂Zn: C, 53.4; H, 4.6; N, 20.7; found C, 53.1; H, 4.4; N, 20.6%. IR $\bar{\nu}_{\text{max}}$ (cm⁻¹): 3307m, 1591m, 1513m, 1482m, 1432m, 1391s, 1319s, 1230s, 1135s, 978m, 909m, 809w, 790s, 743s, 633m.

[Co^{III}(Dp4aT)₂](ClO₄)·3H₂O: Dark brown powder (yield 43%). Anal. Calcd for C₃₀H₃₄ClCoN₁₀O₇S₂: C, 44.7; H, 4.2; N, 17.4; found C, 45.3; H, 4.2; N, 17.4%. IR $\bar{\nu}_{\text{max}}$ (cm⁻¹): 1593m, 1496m, 1414s, 1328m, 1081s, 998m, 781s, 744s, 618s. ¹H NMR (DMSO-d₆): 9.31 (s, 1H, pyr), 8.86 (d, 3H, pyr), 8.74

(s, 1H, pyr); 8.29-8.00 (d, 13H, pyr); 7.81-7.55 (d, 10H, pyr); 5.83-5.76 (m, 3H, -C₃H₅); 5.10 (t, 7H, -C₃H₅); 3.86 (s, 2H, -C₃H₅). ¹³C NMR (DMSO-d₆): 44.0, 113.7, 124, 125, 134.2, 135.1, 148.8, 152.1, 161.4, 164.6 ppm.

Ni^{II}(Dp4aT)₂: Brown powder (yield 69%). Anal. Calcd for C₃₀H₂₈N₁₀ Ni S₂: C, 55.3; H, 4.3; N, 21.5; found C, 54.6; H, 4.2; N, 21.4%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1586m, 1486m, 1430m, 1390s, 1317m, 1229s, 1143s, 919m, 820m, 786s, 741s, 614s.

[Cu^{II}(Dp4aT)₂].5H₂O: Brown powder (yield 67%). Anal. Calcd for C₃₀H₃₈Cu N₁₀O₅S₂: C, 48.2; H, 5.1; N, 18.7; found C, 47.6; H, 4.9; N, 17.9%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1557m, 1507s, 1410s, 1237m, 1079s, 789m, 745m, 619s.

[Zn^{II}(Dp4aT)₂].1.5H₂O: Yellow powder (yield 89%). Anal. Calcd for C₃₀H₃₁N₁₀O_{1.5}S₂Zn: C, 52.5; H, 4.5; N, 20.4; found C, 52.8; H, 4.2; N, 20.5%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 3314m, 1591m, 1514s, 1432m, 1391s, 1319s, 1231s, 1140s, 979s, 910s, 790s, 743s, 615m. ¹H NMR (DMSO-d₆): 9.11 (s, 1H, pyr), 8.83 (d, 3H, pyr), 8.64 (s, 1H, pyr); 8.29-8.00 (d, 13H, pyr); 7.81-7.55 (d, 10H, pyr); 5.81-5.75 (m, 3H, -C₃H₅); 5.10 (t, 7H, -C₃H₅); 3.86 (s, 2H, -C₃H₅). ¹³C NMR (DMSO-d₆): 44.0, 112.1, 123.1, 124.8, 133.4, 134.8, 148.7, 152.1, 162, 164.2 ppm.

[Mn^{II}(Dp4pT)₂].2H₂O: Brown powder (yield 57%). Anal. Calcd for C₃₆H₃₂Mn N₁₀O₂S₂: C, 57.2; H, 4.2; N, 18.5; found C, 57.9; H, 4.2; N, 18.2%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1593m, 1529m, 1491m, 1450m, 1403s, 1315s, 1179m, 1123s, 977m, 812m, 788m, 742s, 682m, 654m, 611m.

[Co^{III}(Dp4pT)₂](ClO₄): Dark brown powder (yield 51%). Anal. Calcd for C₃₆H₂₈ClCoN₁₀O₄S₂: C, 52.5; H, 3.4; N, 17.0; found C, 52.5; H, 3.8; N, 16.8%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1594m, 1491s, 1419s, 1076s, 786m, 744s, 688s, 656m, 618s. ¹H NMR (DMSO-d₆): 10.75 (s, 1H, pyr); 8.92 (d, 1H, pyr); 8.39 (d, 2H, pyr); 8.29 (d, 3H, pyr); 8.07 (t, 2H, pyr); 7.8-7.5 (m, 3H, pyr); 7.46 (d, 3H, aryl); 7.24 (t, 4H, aryl); 7.04 (t, 2H, aryl). ¹³C NMR (DMSO-d₆): 120.7, 123.9, 125.4, 127.4, 128.4, 136.9, 139.2, 140.2, 148.6, 149.7, 156.34, 160.04 ppm.

[Ni^{II}(Dp4pT)₂·H₂O]: Brown powder (yield 62%). Anal. Calcd for C₃₆H₃₀N₁₀NiO₂S₂: C, 58.3; H, 4.0; N, 18.8; found C, 58.5; H, 3.9; N, 18.9%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1590m, 1536m, 1484m, 1393s, 1310s, 1234m, 1177m, 1126s, 977m, 747s, 690m, 655m, 613m.

[Cu^{II}(Dp4pT)₂·0.5H₂O]: Brown powder (yield 56%). Anal. Calcd for C₃₆H₂₉Cu N₁₀O_{0.5}S₂: C, 58.6; H, 3.9; N, 19.0; found C, 58.6; H, 3.8; N, 18.9%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1589m, 1533m, 1483s, 1395s, 1308s, 1248m, 1234m, 1174m, 1128s, 977m, 806m, 749s, 690s, 614m.

[Zn^{II}(Dp4pT)₂·1.5H₂O]: Yellow powder (yield is 78%). Anal. Calcd for C₃₆H₃₁N₁₀ O_{1.5}S₂Zn: C, 57.1; H, 4.1; N, 18.5. Found C, 57.7; H, 3.9; N, 18.9%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1590m, 1535m, 1483m, 1446m, 1390s, 1311s, 1234m, 1177m, 1126s, 976s, 806m, 791m, 744s, 690m, 656m, 513m. ¹H NMR (DMSO-d₆): 10.28 (s, 1H, pyr); 8.94 (d, 1H, pyr); 8.36 (d, 2H, pyr); 8.26 (d, 3H, pyr); 8.01 (t, 2H, pyr); 7.8-7.5 (m, 3H, pyr); 7.46 (d, 3H, aryl); 7.24 (t, 4H, aryl); 7.04 (t, 2H, aryl). ¹³C NMR (DMSO-d₆): 121.2, 123.2, 124.4, 127.1, 127.4, 136.9, 139.2, 140.2, 148.6, 149.7, 156.34, 160.04 ppm.

Mn^{II}(DpT)₂: Brown powder (yield 72%). Anal. Calcd for C₂₄H₂₀Mn N₁₀S₂: C, 50.7; H, 3.5; N, 24.6. Found C, 50.1; H, 3.7; N, 23.9%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1613m, 1590m, 1544m, 1393s, 1314s, 1220m, 1134s, 954m, 787s, 720s, 611m.

[Co^{III}(DpT)₂](ClO₄): Dark brown (yield 45%). Anal. Calcd for C₂₄H₂₀ClCoN₁₀O₄S₂: C, 42.9; H, 3.0; N, 20.8. Found C, 42.1; H, 3.7; N, 19.3%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1627m, 1592m, 1494m, 1423s, 1326s, 1221m, 1150s, 1082s, 998m, 779m, 745m, 619s. ¹H NMR (DMSO-d₆): 8.54 (d, 2H, pyr); 8.44(d, 2H, pyr); 7.95-8.00(m, 3H, pyr); 7.72(t, 1H, pyr); 7.48 (t, 2H, pyr). ¹³C NMR (DMSO-d₆): 122.2, 123.9, 133.8, 146.7, 148.5, 150.5, 159.3, 162.4 ppm.

Ni^{II}(DpT)₂: Brown powder, (yield 57%). Anal. Calcd for C₂₄H₂₀N₁₀Ni S₂: C, 50.4; H, 3.5; N, 24.5. Found C, 49.9; H, 3.5; N, 24.3%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1585s, 1380s, 1296s, 1221m, 1135s, 950m, 785m, 745m, 723s, 612m.

Cu^{II}(DpT)₂: Brown powder (yield 52%). Anal. Calcd for C₂₄H₂₀CuN₁₀S₂: C, 50.0; H, 3.5; N, 24.3. Found C, 49.8; H, 3.3; N, 23.8%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1595m, 1419s, 1322m, 1223m, 1150m, 1083s, 788m, 746m, 618s.

Zn^{II}(DpT)₂: Yellow powder (yield 75%). Anal. Calcd for C₂₄H₂₀N₁₀S₂Zn: C, 49.8; H, 3.4; N, 24.2. Found C, 49.4; H, 3.3; N, 23.7%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1585s, 1473m, 1380s, 1297s, 1222m, 1135s, 950m, 789s, 746m, 721s, 611m. ¹H NMR (DMSO-d₆): 8.56 (d, 2H, pyr); 8.4 (d, 2H, pyr); 7.85-8.00(m, 3H, pyr); 7.75 (t, 1H, pyr); 7.44 (t, 2H, pyr). ¹³C NMR (DMSO-d₆): 120.2, 126.2, 133.8, 146.7, 148.5, 150.5, 159.3, 162.4 ppm.

[Mn^{II}(Dp4eT)₂].2.5H₂O: Brown powder (yield 65%). Anal. Calcd for C₂₈H₃₃MnN₁₀O_{2.5}S₂: C, 50.2; H, 4.9; N, 20.9. Found C, 50.3; H, 4.6; N, 20.6%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1404s, 1324m, 1233s, 1083s, 972m, 790m, 743s, 621s.

[Co^{III}(Dp4eT)₂](ClO₄).2H₂O: Dark brown powder (yield 60%). Anal. Calcd for C₂₈H₃₂ClCoN₁₀O₆S₂: C, 44.0; H, 4.2; N, 18.3. Found C, 44.2; H, 3.9; N, 18.4%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1555m, 1511m, 1422s, 1403m, 1301s, 1275s, 1157m, 1082s, 785m, 744m, 620s. ¹H NMR (DMSO-d₆): 9.14 (s, 1H, pyr); 8.86 (d, 3H, pyr); 8.54 (s, 2H, pyr); 8.3-7.99 (d, 12H, pyr); 7.78-7.52 (d, 9H, pyr); 1.05 (s, 9H, -C₂H₅). ¹³C NMR (DMSO-d₆): 16.2, 33.1, 122.1, 123.6, 133.8, 145.9, 148.5, 162.0, 163.6 ppm.

Ni^{II}(Dp4eT)₂: Brown powder (yield 59%). Anal. Calcd for C₂₈H₂₈N₁₀NiS₂: C, 53.6; H, 4.5; N, 22.3. Found C, 53.2; H, 4.3; N, 22.4%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1586m, 1540m, 1504m, 1452s, 1368s, 1328m, 1235s, 1216s, 1175m, 1155m, 1122s, 1049s, 973m, 783m, 741s, 684m, 612m.

Cu^{II}(Dp4eT)₂: Brown powder (yield 79%). Anal. Calcd for C₂₈H₂₈CuN₁₀S₂: C, 53.1; H, 4.4; N, 22.1. Found C, 53.2; H, 4.5; N, 21.9%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1511m, 1428s, 1246m, 1075s, 784s, 743m, 646m, 621s.

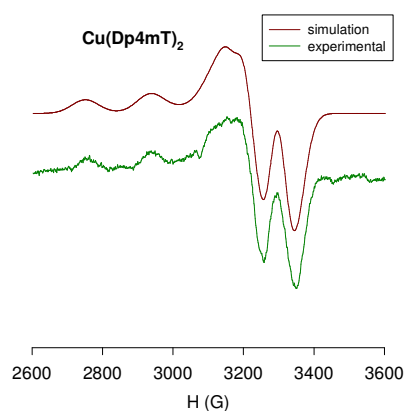
Zn^{II}(Dp4eT)₂: Yellow powder (yield 78%). Anal. Calcd for C₂₈H₂₈N₁₀S₂Zn: C, 53.0; H, 4.4; N, 22.0. Found C, 52.9; H, 4.3; N, 21.2%. IR $\bar{\nu}_{\max}$ (cm⁻¹): 1535s, 1463s, 1325s, 1298m, 1218s, 1160s, 1104m,

1051s, 1005s, 972m, 798s, 724s, 648s. ^1H NMR (DMSO- d_6): 9.01 (s, 1H, pyr); 8.83 (d, 3H, pyr); 8.51 (s, 2H, pyr); 8.1-7.89 (d, 12H, pyr); 7.78-7.52 (d, 9H, pyr); 1.10 (s, 9H, $-\text{C}_2\text{H}_5$). ^{13}C NMR (DMSO- d_6): 18.1, 30.5, 122.1, 123.6, 132.3, 145.9, 148.5, 162, 163.6 ppm.

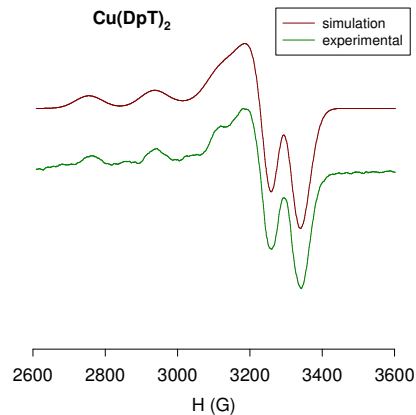
UV-Vis Spectral Data (MeOH solution)

Complexes	Wavelength λ_{max} , nm	Extinction coefficient (ϵ)
Mn(DpT) ₂	279	22 120
	338	20 060
	400	12 630
Mn(Dp4mT) ₂	277	12 670
	336	8 884
	406	8 585
Mn(Dp44mT) ₂	260	11 295
	312	8 940
	418	15 725
Mn(Dp4aT) ₂	280	16 350
	340	17 000
	406	9 280
Mn(Dp4eT) ₂	270	22 835
	301	22 850
	403	11 140
Mn(Dp4pT) ₂	258	22 570
	360	12 025
	410	19 230
[Co(DpT) ₂](ClO ₄)	311	21 370
	367	13 595
	434	7 195
[Co(Dp4mT) ₂](ClO ₄)	261	25 565
	316	16 425
	379	13 590
[Co(Dp44mT) ₂](ClO ₄)	261	27 760
	316	17 815
	389	16 945
[Co(Dp4aT) ₂](ClO ₄)	263	21 940
	316	14 780
	380	13 085
[Co(Dp4eT) ₂](ClO ₄)	263	23 530
	317	14 880
	382	13 385
[Co(Dp4pT) ₂](ClO ₄)	260	39 200
	314	15 630
	412	19 040
Ni(DpT) ₂	267	11 150
	339	5 925
	418	6 020
Ni(Dp4mT) ₂	262	12 080
	358	6 095
	423	6 945
Ni(Dp44mT) ₂	258	19 425

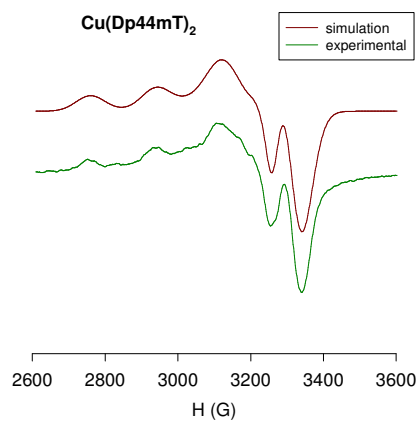
	377 432	12 930 14 850
Ni(Dp4aT) ₂	301 357 425	25 530 23 375 23 760
Ni(Dp4eT) ₂	300 358 424	10 615 9 550 10 350
Ni(Dp4pT) ₂	259 393 429	29 775 21 700 16 725
Cu(DpT) ₂	259 297 398	31 690 30 545 16 635
Cu(Dp4mT) ₂	260 305 411	13 765 13 480 8 035
Cu(Dp44mT) ₂	258 311 403	17 380 15 185 16 190
Cu(Dp4aT) ₂	260 294 417	26 315 24 005 15 640
Cu(Dp4eT) ₂	260 302 426	21 630 20 730 17 625
Cu(Dp4pT) ₂	261 348 399	29 225 18 210 21 260
Zn(DpT) ₂	279 371 397	13 345 5 810 7 870
Zn(Dp4mT) ₂	263 288 416	13 090 10 795 14 815
Zn(Dp44mT) ₂	263 293 416	13 030 10 345 14 795
Zn(Dp4aT) ₂	260 303 405	20 615 22 805 30 530
Zn(Dp4eT) ₂	262 361 409	12 460 12 210 15 190
Zn(Dp4pT) ₂	257 361 409	28 685 16 675 26 795



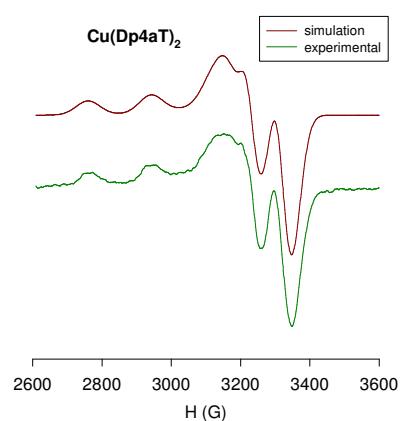
$g_x=2.048$ ($A_x=9\text{G}$), $g_y=2.065$ ($A_y=18\text{G}$), $g_z=2.191$ ($A_z=182\text{G}$)



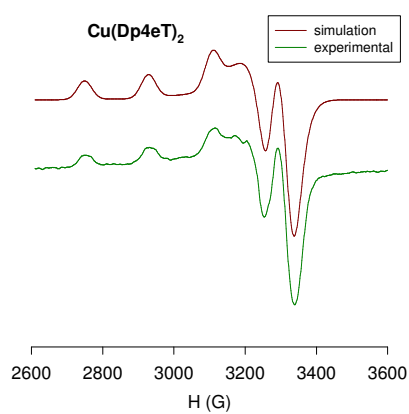
$g_x=2.047$ ($A_x=5\text{G}$), $g_y=2.067$ ($A_y=17\text{G}$), $g_z=2.199$ ($A_z=179\text{G}$)



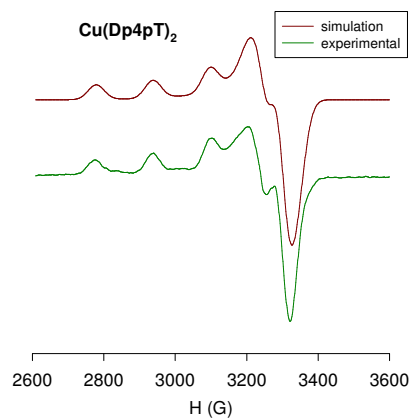
$g_x=2.051$ ($A_x=6\text{G}$), $g_y=2.086$ ($A_y=50\text{G}$), $g_z=2.193$ ($A_z=180\text{G}$)



$g_x=2.040$ ($A_x=3\text{G}$), $g_y=2.066$ ($A_y=30\text{G}$), $g_z=2.193$ ($A_z=181\text{G}$)



$g_x=2.048$ ($A_x=9\text{G}$), $g_y=2.059$ ($A_y=18\text{G}$), $g_z=2.200$ ($A_z=180\text{G}$)



$g_x=2.037$ ($A_x=19\text{G}$), $g_y=2.057$ ($A_y=12\text{G}$), $g_z=2.202$ ($A_z=159\text{G}$)

Fig. S1. EPR (experimental and simulated) spectra of Cu^{II} complexes. Spin Hamiltonian parameters shown.

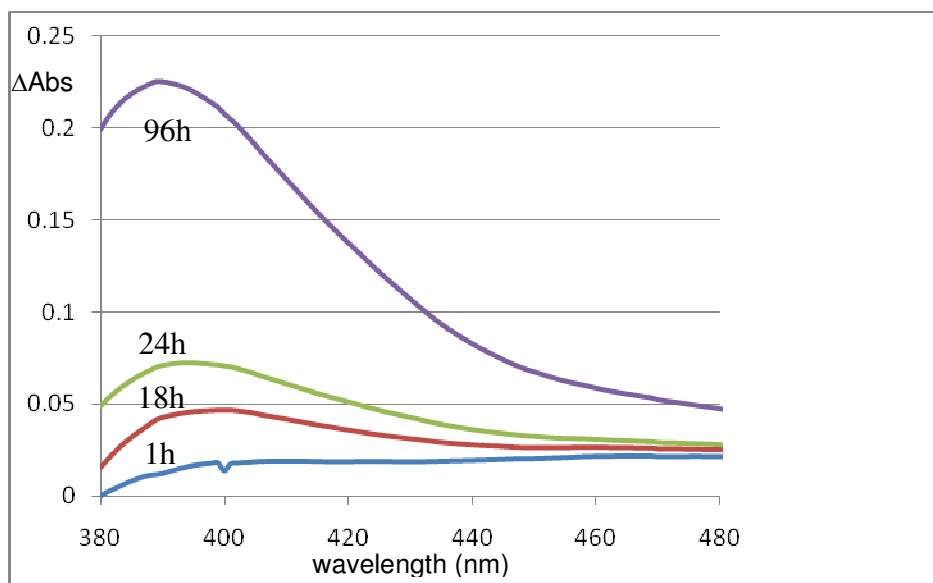


Fig. S2. Difference absorption spectra showing formation of $[\text{Fe}^{\text{III}}(\text{Dp44mT})_2]^{3+}$ (λ_{max} 390 nm) as the product of reaction between $[\text{Fe}^{\text{III}}(\text{DFO})]^+$ and a 20-fold excess of **HDp44mT**. Experimental conditions: ferrioxamine solution (2 mL, 100 μM) plus DMSO (600 μL) and 20-fold molar excess of **HDp44mT** at pH 7.4. Spectra were measured 1 h, 18 h, 24 h and 96 h after mixing.