MATERIAL SUPPORTING TO

Spectrophotometric Determination of Formation Constants of Iron(III) Complexes with Several Ligands

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Table S1. Summary of experimental parameters for the systems Fe^{3+} with ethylenediamine (*en*), 1,3-diaminopropane (*pn*) and 1,4-diaminopropane (*bn)* in methanol.

Solution composition		$[T_L]$ range from 11.9 to 238.0 and 104.8 to 419.3 μmol L^{-1}		
		$[T_M]$ constant at 118.8 and 198 μmol L^{-1}		
		Ionic strength, electrolyte	Not used	
		pH range	Not used	
Experimental method		Spectrophotometric titration		
Temperature		298 K		
Total number of data points		Fe complexation: 28 solution spectra		
Method of calculation		HypSpec		
Species	Equilibrium		Log β	σ
$[Fe(en)]^{3+}$	Fe^{3+}+ en ⇄ $[Fe(en)]^{3+}$		$\log \beta_{110} = 5.3 \pm 0.2$	0.0017
$[Fe(en)_2]^{3+}$	Fe^{3+}+2 en ⇄ $[Fe(en)_2]^{3+}$		$\log \beta_{120} = 10.9 \pm 0.1$	
Solution composition		$[T_L]$ range from 13.2 to 263.6 and 63.2 to 421.6 μmol L^{-1}		
		$[T_M]$ constant at 118.8 and 198 μmol L^{-1}		
		Ionic strength, electrolyte	Not used	
		pH range	Not used	
Experimental method		Spectrophotometric titration		
Temperature		298 K		
Total number of data points		Fe complexation: 29 solution spectra		
Method of calculation		HypSpec		
Species	Equilibrium		Log β	σ
$[Fe(pn)]^{3+}$	Fe^{3+}+ pn ⇄ $[Fe(pn)]^{3+}$		$\log \beta_{110} = 6.9 \pm 0.2$	0.0072
$[Fe(pn)_2]^{3+}$	Fe^{3+}+2 pn ⇄ $[Fe(pn)_2]^{3+}$		$\log \beta_{120} = 12.4 \pm 0.1$	
Solution composition		$[T_L]$ range from 11.9 to 202.9 and 23.9 to 406.0 μmol L^{-1}		
		$[T_M]$ constant at 118.8 and 198 μmol L^{-1}		
		Ionic strength, electrolyte	Not used	
		pH range	Not used	
Experimental method		Spectrophotometric titration		
Temperature		298 K		
Total number of data points		Fe complexation: 29 solution spectra		
Method of calculation		HypSpec		
Species	Equilibrium		Log β	σ
$[Fe(bn)]^{3+}$	Fe^{3+}+ bn ⇄ $[Fe(bn)]^{3+}$		$\log \beta_{110} = 5.2 \pm 0.1$	0.0057
$[Fe(bn)_2]^{3+}$	Fe^{3+}+2 bn ⇄ $[Fe(bn)_2]^{3+}$		$\log \beta_{120} = 10.2 \pm 0.1$	

Table S2. Summary of experimental parameters for the systems Fe^{3+} with 2,2'-bipyridyl(*bipy*), 5,5′-dimetyl-2,2'-bipyridyl (*dmbipy*) and 4,4'-di-tert-butyl-2,2'-bipyridyl (*dtbbipy*)in methanol.

Solution composition	$[T_L]$ range from 3.072 to 30.72 and 4.6 to 92 μmol L^{-1}		
	$[T_M]$ constant at 9.9 and 29.64 μmol L^{-1}		
	Ionic strength, electrolyte		Not used
	pH range		Not used
Experimental method	Spectrophotometric titration		
Temperature	298 K		
Total number of data points	Fe complexation: 37 solution spectra		
Method of calculation	HypSpec		
Species	Equilibrium	Log β	σ
$[Fe(Bipy)]^{3+}$	Fe^{3+}+ Bipy ⇄ $[Fe(Bipy)]^{3+}$	$\log \beta_{110}$ = 5.2 ± 0.1	
$[Fe(Bipy)_2]^{3+}$	Fe^{3+}+2 Bipy ⇄ $[Fe(Bipy)_2]^{3+}$	$\log \beta_{120}$ = 10.3 ± 0.1	0.0040
$[Fe(Bipy)_3]^{3+}$	Fe^{3+}+3 Bipy ⇄ $[Fe(Bipy)_3]^{3+}$	$\log \beta_{130}$ = 15.0 ± 0.1	

Solution composition	$[T_L]$ range from 1.04 to 20.8 and 2.08 to 41.6 μmol L^{-1}		
	$[T_M]$ constant at 9.9 and 19.8 μmol L^{-1}		
	Ionic strength, electrolyte		Not used
	pH range		Not used
Experimental method	Spectrophotometric titration		
Temperature	298 K		
Total number of data points	Fe complexation: 40 solution spectra		
Method of calculation	HypSpec		
Species	Equilibrium	Log β	σ
$[Fe(dmBipy)]^{3+}$	Fe^{3+}+dmBipy ⇄ $[Fe(dmBipy)]^{3+}$	$\log \beta_{110}$ = 5.8 ± 0.1	0.0063
$[Fe(dmBipy)_2]^{3+}$	Fe^{3+}+2 dmBipy ⇄ $[Fe(dmBipy)_2]^{3+}$	$\log \beta_{120}$ =11.0 ± 0.1	

Solution composition	$[T_L]$ range from 2.086 to 20.86 and 2.086 to 41.72 μmol L^{-1}		
	$[T_M]$ constant at 9.9 and 19.8 μmol L^{-1}		
	Ionic strength, electrolyte		Not used
	pH range		Not used
Experimental method	Spectrophotometric titration		
Temperature	298 K		
Total number of data points	Fe complexation: 39 solution spectra		
Method of calculation	HypSpec		
Species	Equilibrium	Log β	σ
$[Fe(dtbBipy)]^{2+}$	Fe^{3+}+dtbBipy⇄ $[Fe(dtbBipy)]^{2+}$	$\log \beta_{110}$ = 6.5 ± 0.1	0.0044
$[Fe(dtbBipy)_2]^{2+}$	Fe^{3+}+2dtbBipy ⇄$[Fe(dtbBipy)_2]^{2+}$	$\log \beta_{120}$ = 12.2 ± 0.1	

Table S3. Summary of experimental parameters for the systems Fe^{3+} with 1,10-phenanthroline (*phen*) and 3,4,7,8-tetramethyl-1,10-phenanthroline (*tmPhen*) in methanol.

Solution composition	$[T_L]$ range from 0.73 to 14.6 and 0.955 to 19.1 μmol L^{-1}		
	$[T_M]$ constant at 4.74 and 5.9 μmol L^{-1}		
	Ionic strength, electrolyte		Not used
	pH range		Not used
Experimental method	Spectrophotometric titration		
Temperature	298 K		
Total number of data points	Fe complexation: 39 solution spectra		
Method of calculation	HypSpec		
Species	Equilibrium	Log β	σ
$[Fe(Phen)]^{3+}$	Fe^{3+} + Phen ⇄ $[Fe(Phen)]^{3+}$	$\log \beta_{110} = 6.1 \pm 0.1$	
$[Fe(Phen)_2]^{3+}$	Fe^{3+}+2 Phen ⇄ $[Fe(Phen)_2]^{3+}$	$\log \beta_{120} = 12.2 \pm 0.1$	0.0071
$[Fe(Phen)_3]^{3+}$	Fe^{3+}+3 Phen ⇄ $[Fe(Phen)_3]^{3+}$	$\log \beta_{130} = 17.6 \pm 0.1$	
Solution composition	$[T_L]$ range from 0.305 to 6.092 and 0.609 to 12.184 μmol L^{-1}		
	$[T_M]$ constant at 2.934 and 5.868 μmol L^{-1}		
	Ionic strength, electrolyte		Not used
	pH range		Not used
Experimental method	Spectrophotometric titration		
Temperature	298 K		
Total number of data points	Fe complexation: 40 solution spectra		
Method of calculation	HypSpec		
Species	Equilibrium	Log β	σ
$[Fe(tmPhen)]^{3+}$	Fe^{3+} + tmPhen ⇄ $[Fe(tmPhen)]^{3+}$	$\log \beta_{110} = 5.4 \pm 0.1$	0.0038
$[Fe(tmPhen)_2]^{3+}$	Fe^{3+}+2 tmPhen ⇄ $[Fe(tmPhen)_2]^{3+}$	$\log \beta_{120} = 10.6 \pm 0.1$	

Table S4. Equilibrium constants for Fe^{3+} systems with 2,2'- bipyridine and 1,10-phenanthroline, under different conditions.

Method	Solvent	Ionic Strength	T(°C)	$Log\beta_{110}$	$Log\beta_{120}$	$Log\beta_{130}$	Reference
2,2'-bipyridine							
Espectrophotometic	Water	_	25	_	_	17.39	[37]
Potentiometric	Water	0.1 M $NaNO_3$	25	9.13	18.11	_	[36]
1,10-phenanthroline							
Potentiometric	_	_	25	6.5	11.4		[38]
Potentiometric	Agua	0.1 M $NaNO_3$	25	10.41	19.92	_	[36]

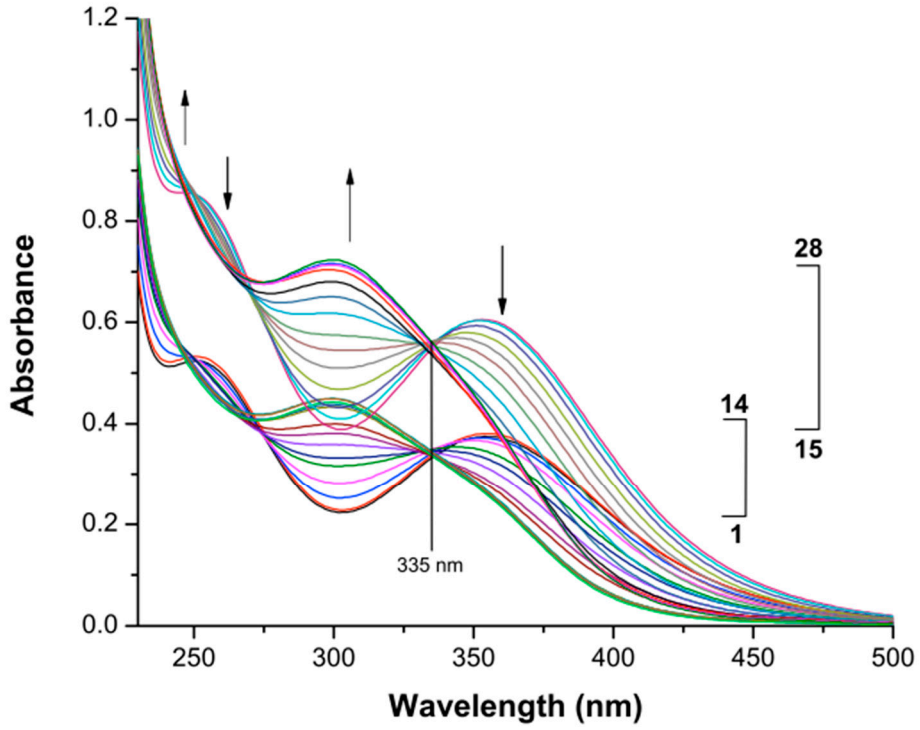

Figure S1. Absorption spectra of iron(III)-ethylenediamine complexes in methanol solution, with an isosbestic point at 335 nm For spectra 1 to 14, [Fe(III)] = 118.8 µM and ethylenediamine concentration (µM): (1) 11.9; (2)23.8; (3) 71.4; (4) 95.2; (5) 119.0; (6) 130.9; (7) 142.8; (8) 154.7; (9) 166.6; (10) 190.4; (11) 202.3; (12) 214.2; (13) 226.1; (14) 238.0. For spectra 15 to 28, [Fe(III)] = 198 µM and ethylenedimine concentration (µM): (15)104.8; (16) 125.8; (17) 146.7; (18) 167.7; (19) 188.6; (20) 209.6; (21) 230.6; (22) 251.5; (23) 272.5; (24) 293.4; (25) 314.4; (26) 377.3; (27) 398.2; (28) 419.2.

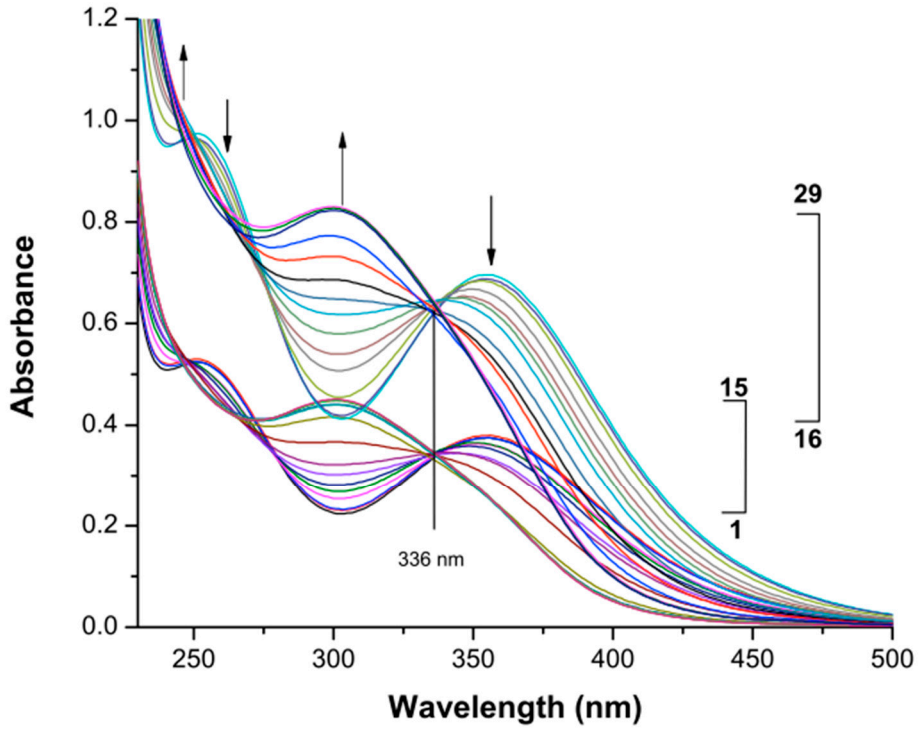

Figure S2. Absorption spectra of iron(III)-1,3-diaminopropane complexes in methanol solution, with an isosbestic point at 336 nm. For spectra 1 to 15, [Fe(III)] = 118.8 μM and 1,3-diaminopropane concentration (μM): (1) 13.2; (2) 26.4; (3) 39.5; (4) 79.1; (5) 92.3; (6) 105.4; (7) 118.6; (8) 131.8; (9) 158.2; (10) 184.5; (11) 210.9; (12) 224.1; (13) 237.2; (14) 250.4; (15) 263.6. For spectra 16 to 29, [Fe(III)] = 198 μM and 1,3-diaminopropane concentration from (μM): (16) 63.2; (17) 105.4) (18) 147.6; (19) 189.7; (20) 210.8; (21) 231.9; (22) 253.0; (23) 274.0; (24) 295.1; (25) 316.2; (26)337.3; (27) 379.4; (28) 400.5; (29) 421.6.

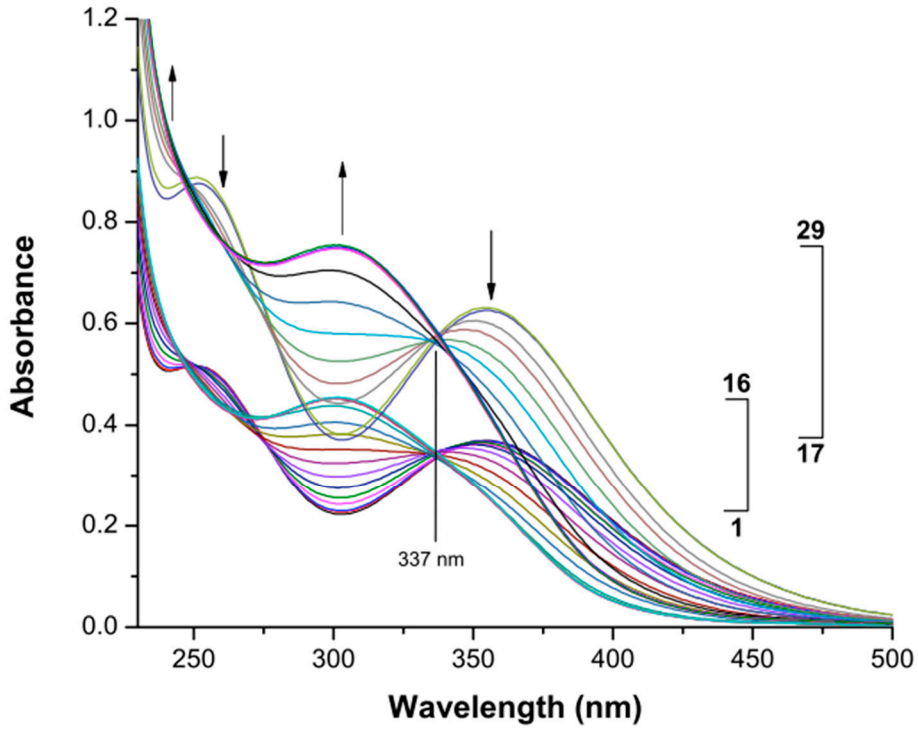

Figure S3. Absorption spectra of iron(III)-1,4-diaminobutane complexes in methanol solution, with an isosbestic point at 337 nm. For spectral 1 to 16, [Fe(III)] = 0.16μM and 1,4-diaminobutane concentration (μM): (1)11.9; (2)23.9; (3) 35.8; (4) 48.8; (5) 59.7; (6) 71.6; (7) 83.6; (8) 95.5; (9) 107.5; (10) 119.4; (11) 131.3; (12) 143.3; (13) 167.2; (14) 179.1; (15) 191.1; (16) 202.9. For spectra 17 to 29, [Fe(III)] = 198 μM and 1,4-diaminobutane concentration (μM): (17) 23.9; (18) 47.8; (19) 119.4; (20) 143.3; (21) 167.2; (22) 191.0; (23) 214.9; (24) 238.8; (25) 310.4; (26) 334.3; (27) 358.2; (28) 382.1; (29) 406.0.

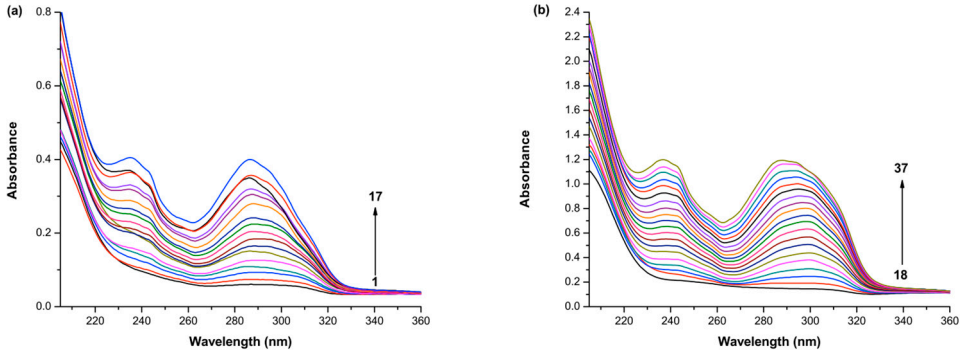

Figure S4. Absorption spectra of iron(III)–2,2'-bipyridyl complex in methanol solution. (**a**) For spectra 1 to 17, [Fe(III)]= 9.9 µM and 2,2'-bipyridyl concentration (µM): (1) 3.072; (2) 4.608; (3) 6.144; (4) 7.68; (5) 9.216; (6) 10.752; (7) 12.288; (8) 13.824; (9) 15.36; (10) 16.896; (11) 18.432; (12) 21.504; (13) 23.04; (14) 24.576; (15) 26.112; (16) 27.648; (17) 30.72. (**b**) For spectra 18 to 37, [Fe(III)]= 29.64 µM and 2,2'-Bipyridyl concentration (µM): (18) 4.6; (19) 9.2; (20) 13.8; (21) 18.4; (22) 23; (23) 27.6; (24) 32.2; (25) 36.8; (26) 41.4; (27) 46; (28) 50.6; (29) 55.2; (30) 59.8; (31) 64.4; (32) 69; (33) 73.6; (34) 78.2; (35) 82.8; (36) 87.4; (37) 92.

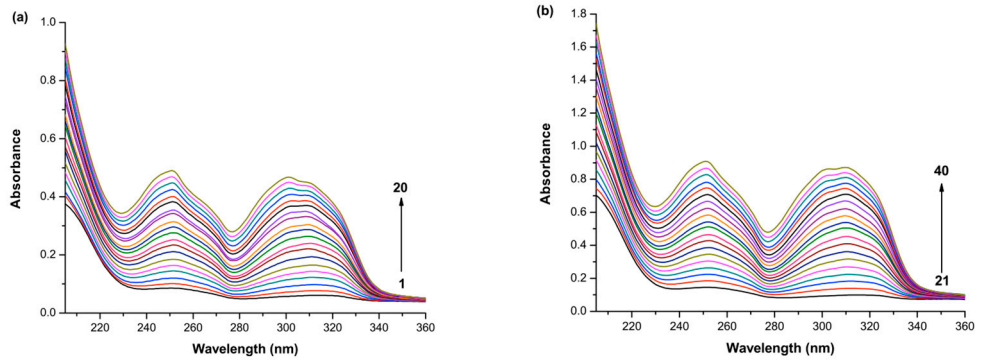

Figure S5. Absorption spectra of iron(III)–5,5-dimetyl-2,2'-bipyridyl complex in methanol solution. (**a**) For spectra 1 to 20, [Fe(III)]= 9.9 µM and 5,5-dimetyl-2,2'-bipyridyl concentration (µM): (1) 1.04; (2) 2.08; (3) 3.12; (4) 4.16; (5) 5.2; (6) 6.24; (7) 7.28; (8) 8.32; (9) 9.36; (10) 10.4; (11) 11.44; (12) 12.48; (13) 13.52; (14) 14.56; (15) 15.6; (16) 16.64; (17) 17.68; (18) 18.72; (19) 19.76; (20) 20.8. (**b**) For spectra 21 to 40, [Fe(III)]= 19.8 µM and 5,5-dimetyl-2,2'-Bipyridyl concentration (µM): (21) 2.08; (22) 4.16; (23) 6.24; (24) 8.32; (25) 10.4; (26) 12.48; (27) 14.56; (28) 16.64; (29) 18.72; (30) 20.8; (31) 22.88; (32) 24.96; (33) 27.04; (34) 29.12; (35) 31.2; (36) 33.28; (37) 35.36; (38) 37.44; (39) 39.52; (40) 41.6.

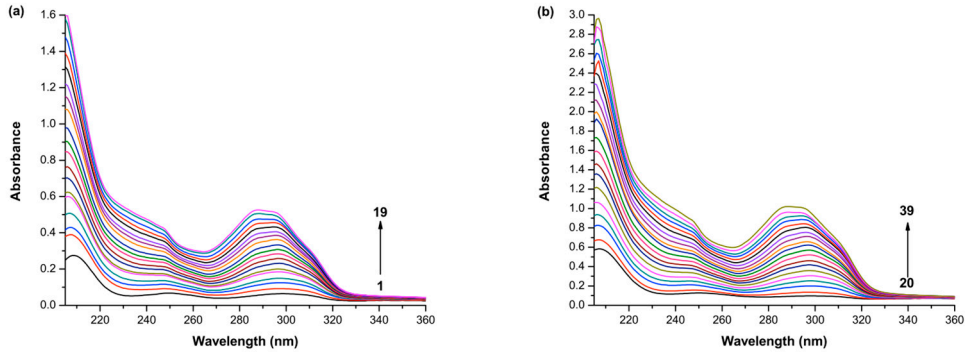

Figure S6. Absorption spectra of iron(III)–4,4'-di-tert-butyl-2,2'-bipyridyl complex in methanol solution. (**a**) For spectra 1 to 20, [Fe(III)]= 9.9 µM and 4,4'-di-tert-butyl-2,2'-bipyridyl concentration (µM): (1) 2.086; (2) 3.129; (3) 4.172; (4) 5.215; (5) 6.258; (6) 7.301; (7) 8.344; (8) 9.387; (9) 10.43; (10) 11.473; (11) 12.516; (12) 13.559; (13) 14.602; (14) 15.645; (15) 16.688: (16) 17.731; (17) 18.774; (18) 19.817; (19) 20.86. (**b**) For spectra 20 to 39, [Fe(III)]= 19.8 µM and 4,4'-di-tert-butyl-2,2'-bipyridyl concentration (µM): (20) 2.086; (21) 4.172; (22) 6.258; (23) 8.344; (23) 10.43; (24) 12.516; (25) 14.602; (26) 16.688; (27) 18.774; (28) 20.86; (29) 22.946; (30) 25.032; (31) 27.118; (32) 29.204; (33) 31.29; (34) 33.376; (35) 35.462; (36) 37.548; (37) 39.634; (38) 41.72; (39) 41.72.

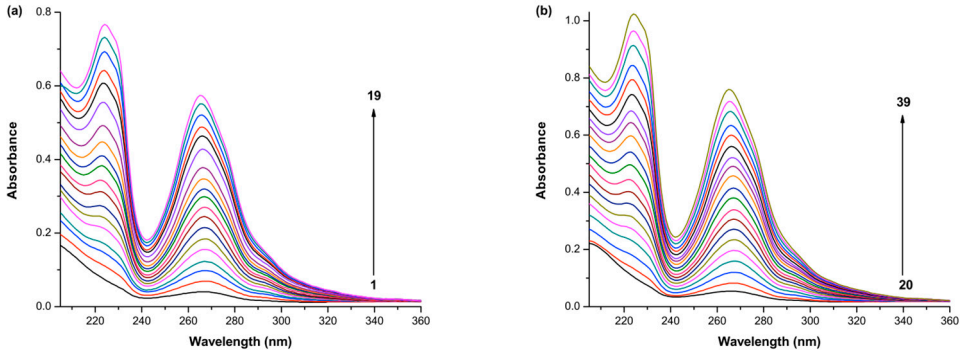

Figure S7. Absorption spectra of iron(III)–1,10-Phenanthroline complex in methanol solution. (**a**) For spectra 1 to 19, [Fe(III)]= 4.74 µM and 1,10-Phenanthroline concentration (µM): (1) 0.73; (2) 1.46; (3) 2.19; (4) 2.92; (5) 3.65; (6) 4.38; (7) 5.11; (8) 5.84; (9) 6.57; (10) 7.3; (11) 8.03; (12) 8.76; (13) 9.49; (14) 10.95; (15) 11.68; (16) 12.41; (17) 13.14; (18) 13.87; (19) 14.6. (**b**) For spectra 20 to 29, [Fe(III)]= 5.9 µM and 1,10-Phenanthroline concentration (µM): (20) 0.955; (21) 1.91; (22) 2.865; (23) 3.82; (24) 4.775; (25) 5.73; (26) 6.685; (27) 7.64; (28) 8.595; (29) 9.55; (30)10.505; (31) 11.46; (32) 12.415; (33) 13.37; (34) 14.325; (35) 15.28; (36) 16.235; (37) 17.19; (38) 18.145; (39)19.1.

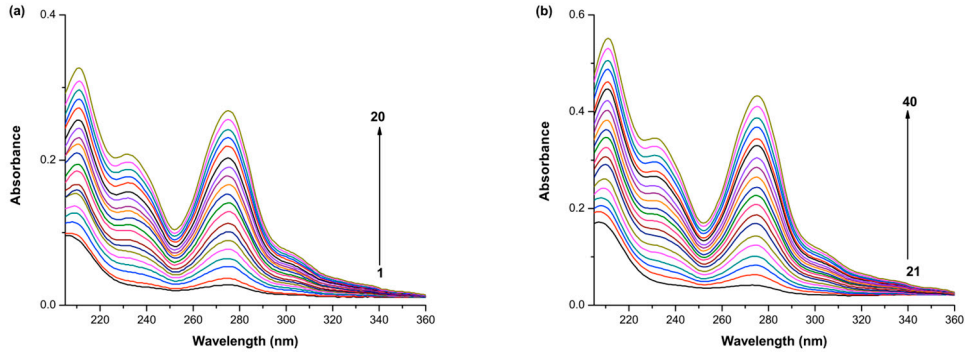

Figure S8. Absorption spectra of iron(III)–3,4,7,8-tetramethyl-1,10-Phenanthroline complex in methanol solution. (**a**) For spectra 1 to 20, [Fe(III)]= 2.934 µM and 3,4,7,8-Tetramethyl-1,10-Phenanthroline concentration (µM): (1) 0.305; (2) 0.609; (3) 0.914; (4) 1.218; (5) 1.523; (6) 1.828; (7) 2.132; (8) 2.437; (9) 2.741; (10) 3.046; (11) 3.351; (12) 3.655; (13) 3.960; (14) 4.264; (15) 4.569; (16) 4.874; (17) 5.178; (18) 5.483; (19) 5.787; (20) 6.092. (**b**) For spectra 21 to 40, [Fe(III)]= 5.868 µM and 3,4,7,8-Tetramethyl-1,10-Phenanthroline concentration (µM): (21) 0.609; (22) 1.218; (23) 1.828; (24) 2.437; (25) 3.046; (26) 3.655; (27) 4.264; (28) 4.874; (29) 5.483; (30) 6.092; (31) 6.701; (32) 7.310; (33) 7.920; (34) 8.529; (35) 9.138; (36) 9.747; (37) 10.356; (38) 10.966; (39) 11.575; (40) 12.184.

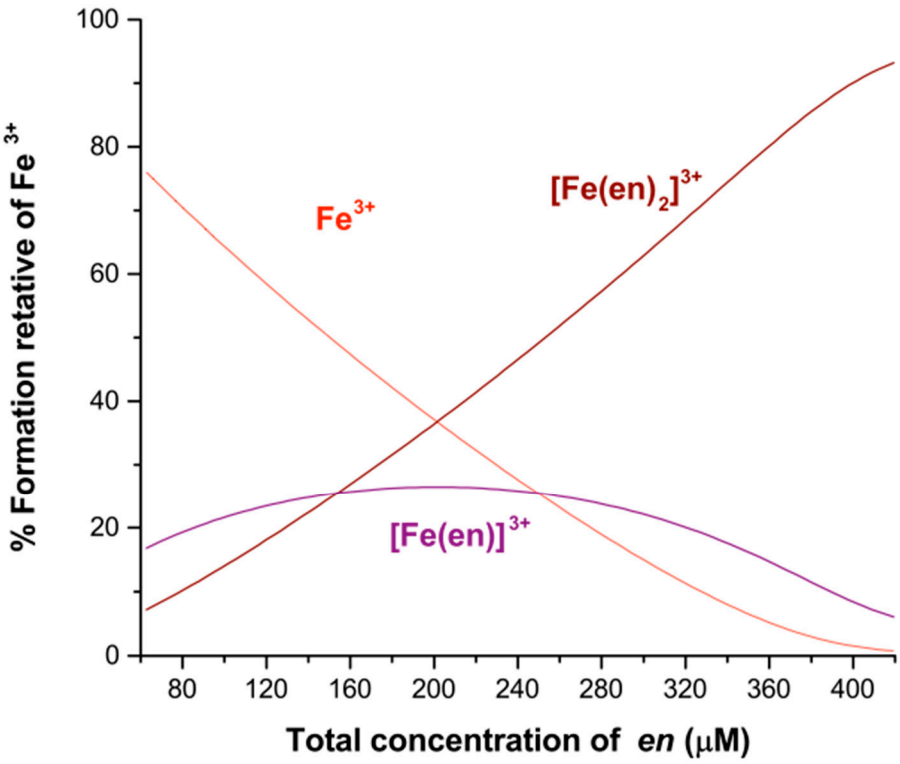

Figure S9. Formation curves of the iron(III)-ethylenediamine system in methanol. $[Fe]^{3+}$ = 198 μM and ethylenediamine range from 62 to 420 μM.

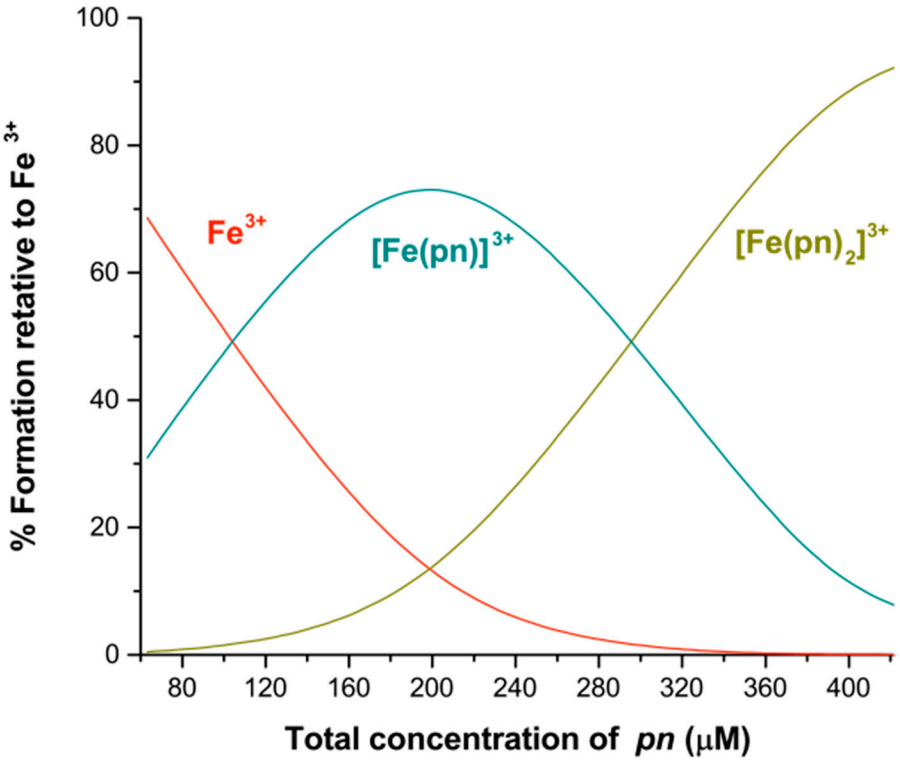

Figure S10. Formation curves of the iron(III)-1,3-propanediamine system in methanol. $[Fe]^{3+}$ = 198 μM and 1,3-propanediamine range from 63 to 0.420 μM.

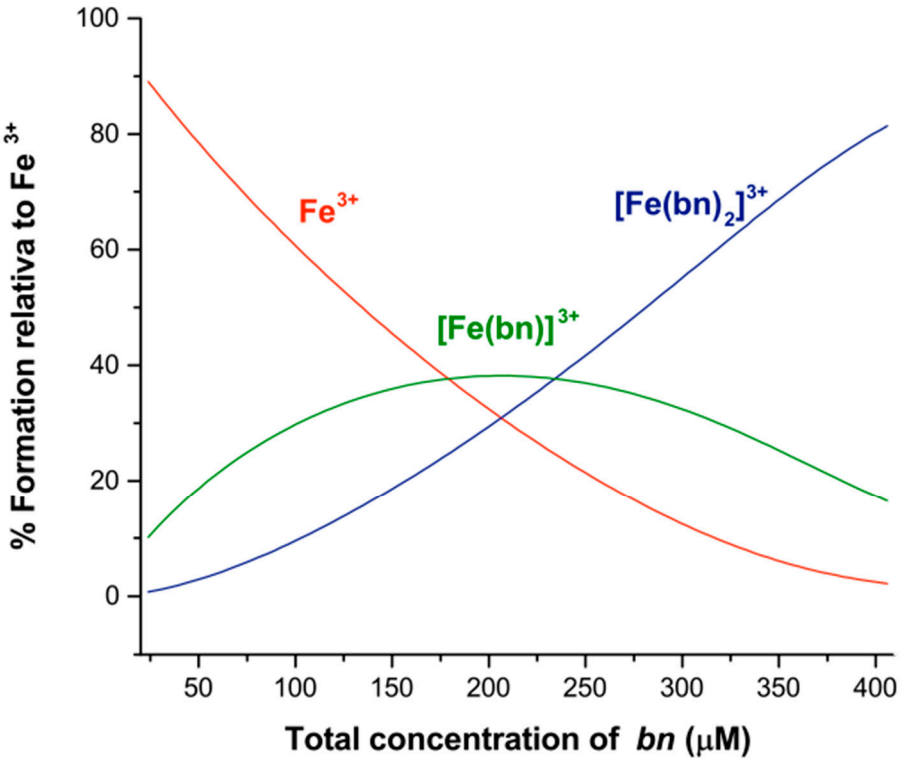

Figure S11. Formation curves of the iron(III)-1,4-butanediamine system in methanol. $[Fe]^{3+}$ = 198 μM y 1,4-butanediamine range from 24 to 406 μM.

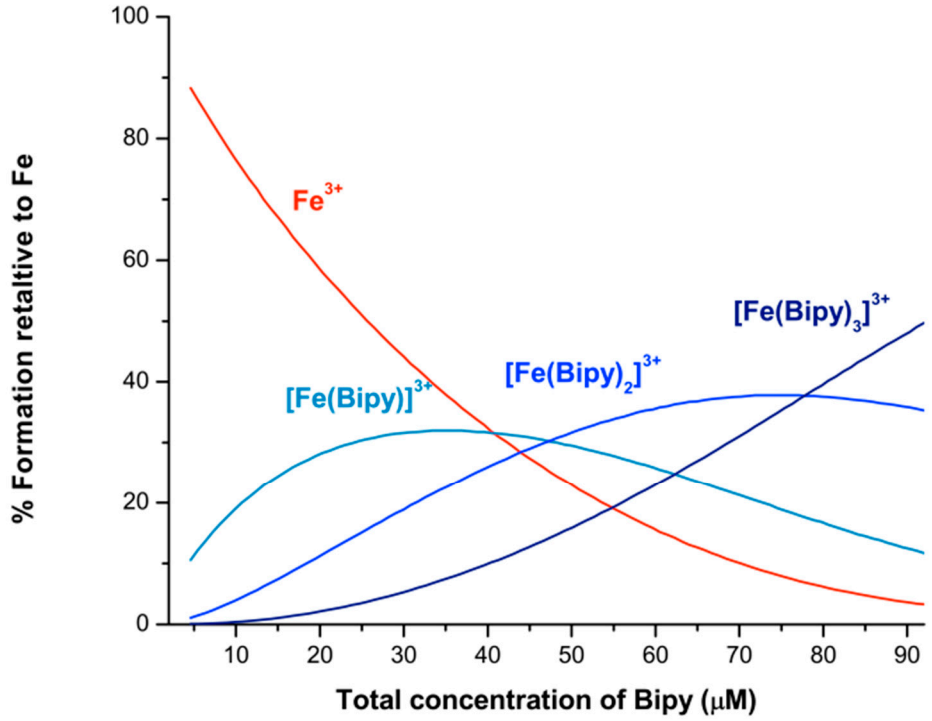

Figure S12. Formation curves of the Fe(III)–2,2'-bipyridyl complex in methanol. $[Fe]^{3+}$ = 29.64 μM and 2,2'-Bipyridyl range from 4.6 to 92 μM.

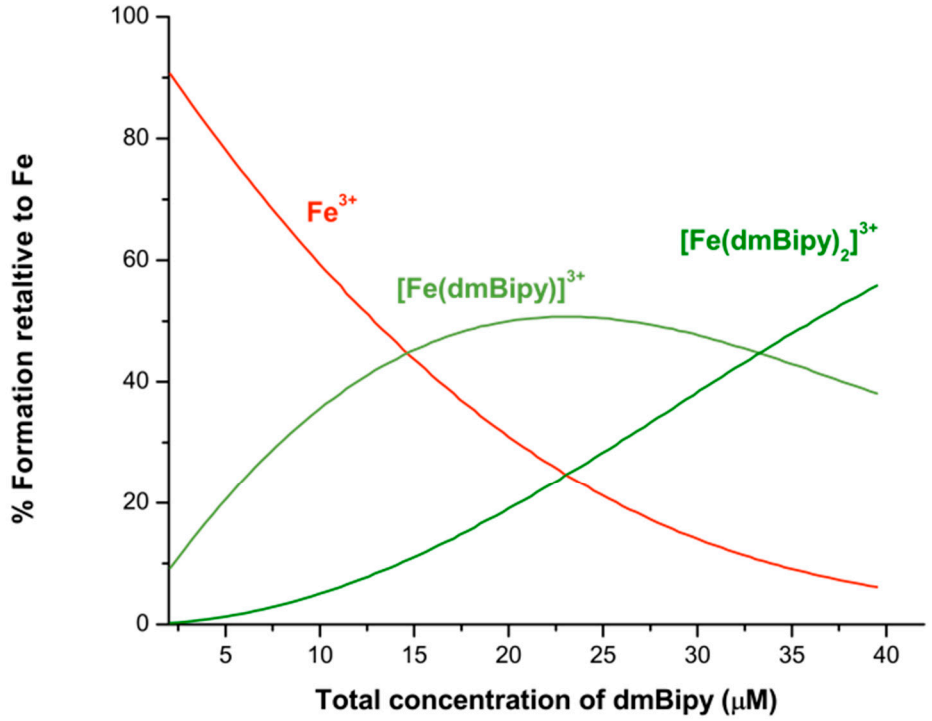

Figure S13. Formation curves of the Fe(III)–5,5′-dimetyl-2,2'-bipyridyl complex in methanol. $[Fe]^{3+}$ = 19.8 μM and 5,5′-dimetyl-2,2'-bipyridyl range from 2.08 to 41.6 μM.

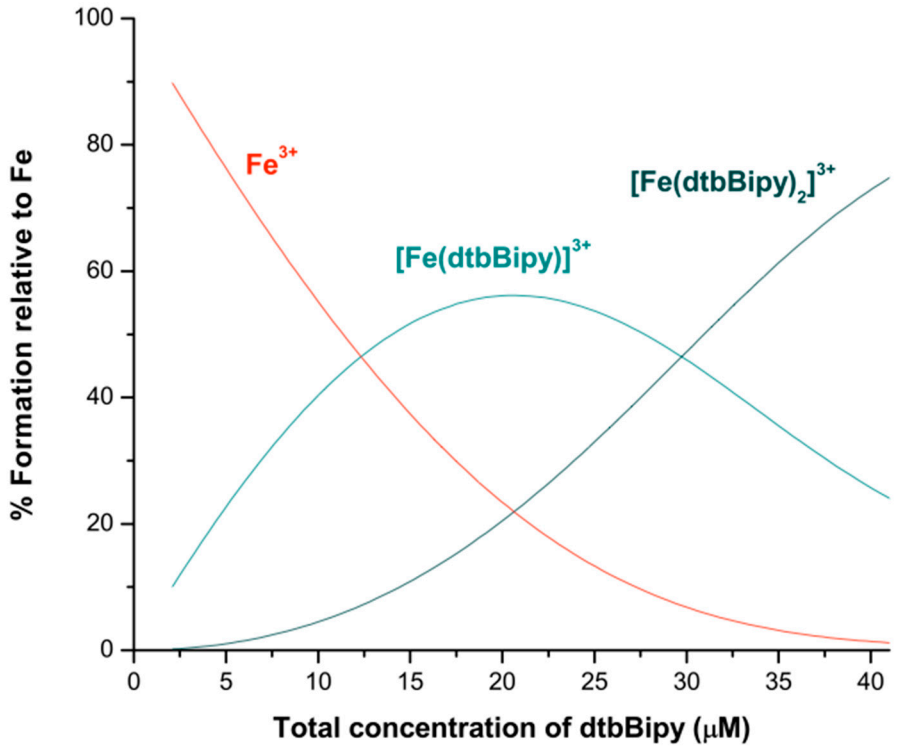

Figure S14. Formation curves of the Fe(III)–4,4'-di-tert-butyl-2,2'-bipyridyl complex in methanol. $[Fe]^{3+}$ = 19.8 μM and 4,4'-di-tert-butyl-2,2'-bipyridyl range from 2.086 to 41.72 μM.

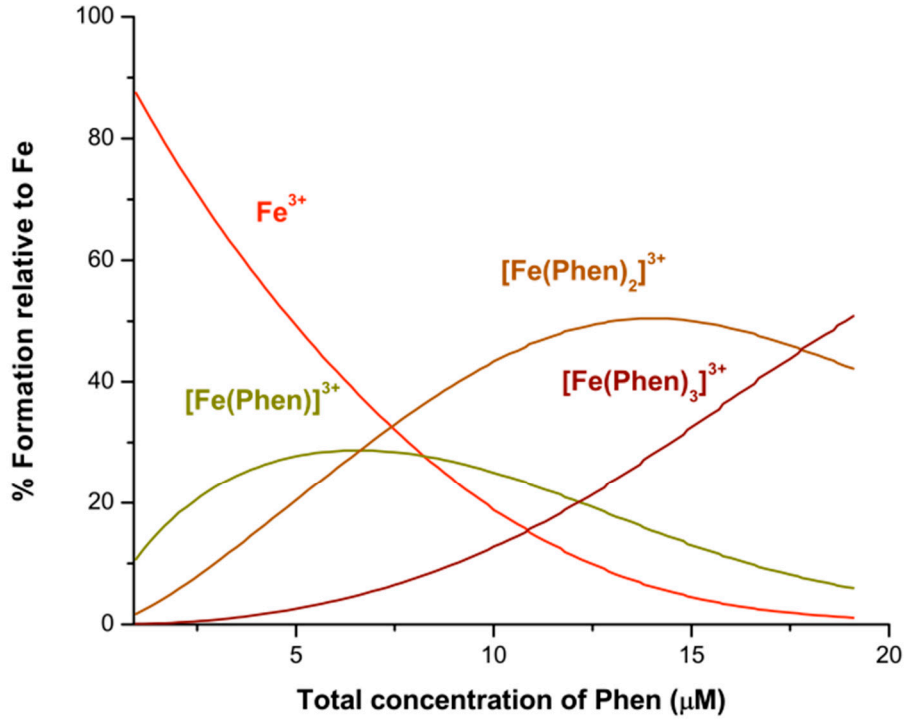

Figure S15. Formation curves of the Fe(III)–1,10-phenanthroline complex in methanol. $[Fe]^{3+}$ = 5.9 μM and 1,10-phenanthroline range from 0.955 to 19.1 μM.

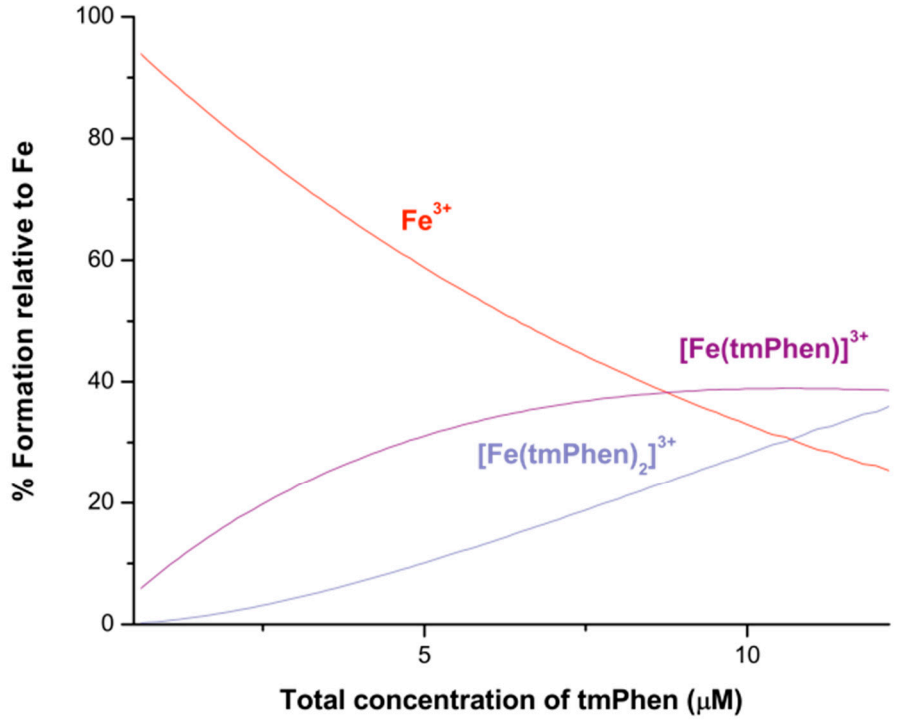

Figure S16. Formation curves of the Fe(III)– 3,4,7,8-tetramethyl-1,10-phenanthroline complex in methanol. $[Fe]^{3+}$ = 5.86 μM and 3,4,7,8-tetramethyl-1,10-phenanthroline range from 0.6092 to 12.18 μM.

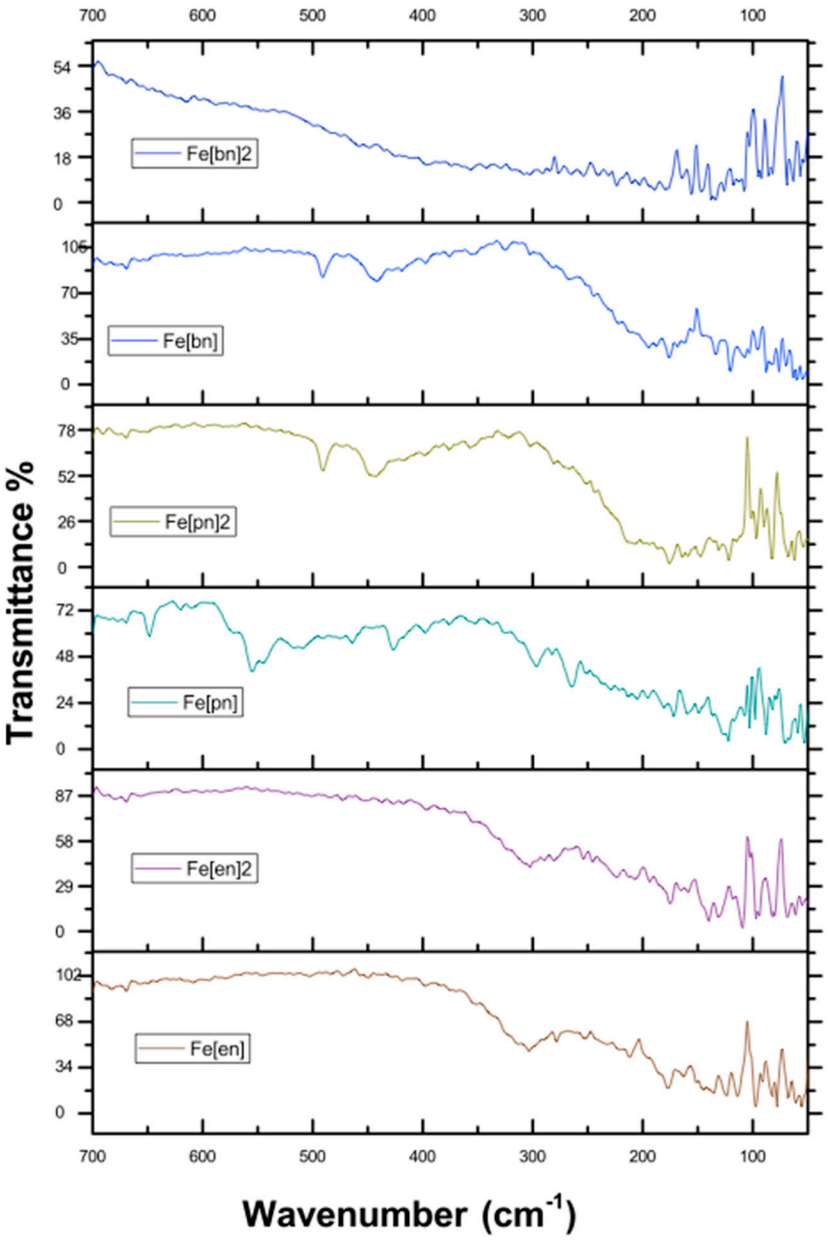

Figure S17. Far infrared spectra of the different Fe(III) complexes with ethylenediamine, 1,3-propanediamine and 1,4-butanediamine.

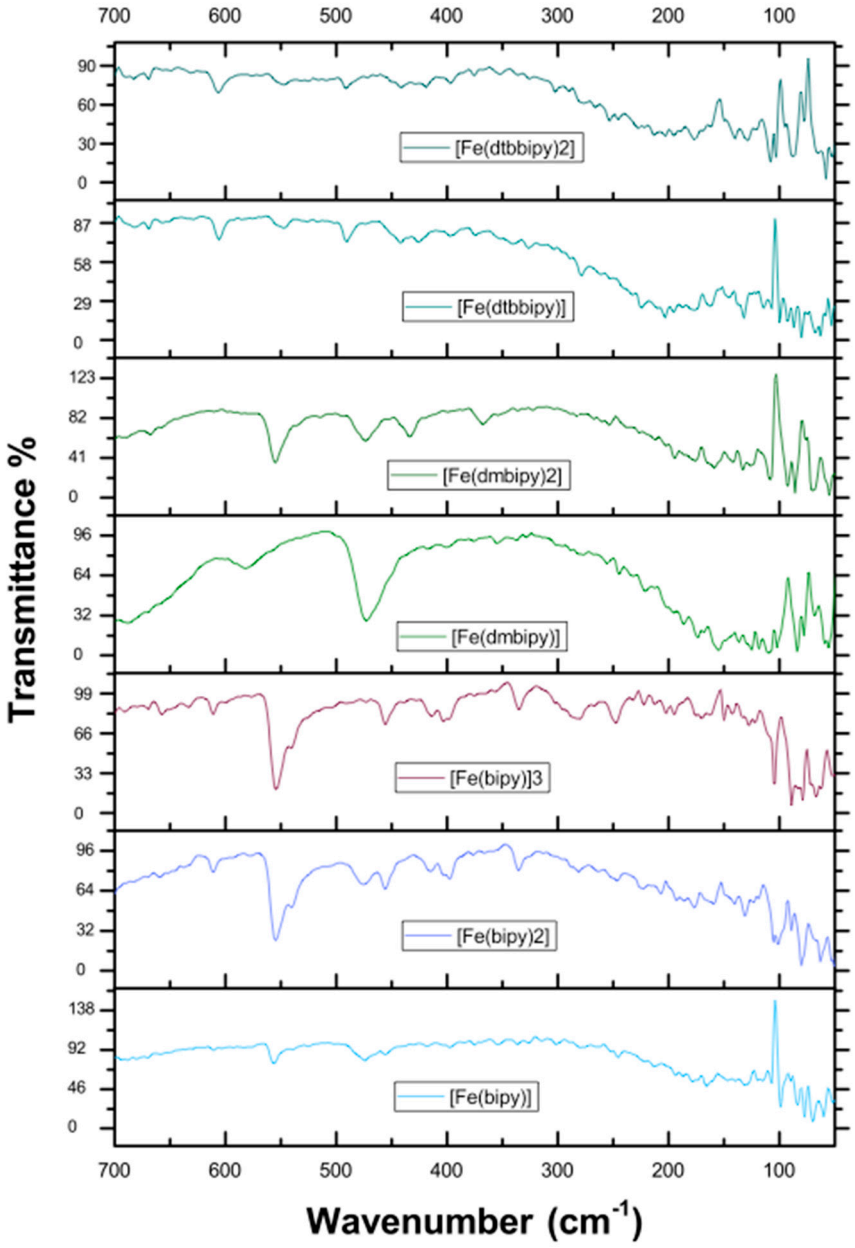

Figure S18. Far infrared spectra of the different Fe(III) complexes with 2,2'-bipyridyl, 5,5-dimetyl-2,2'-bipyridyl, 4,4'-di-tert-butyl-2,2'-bipyridyl.

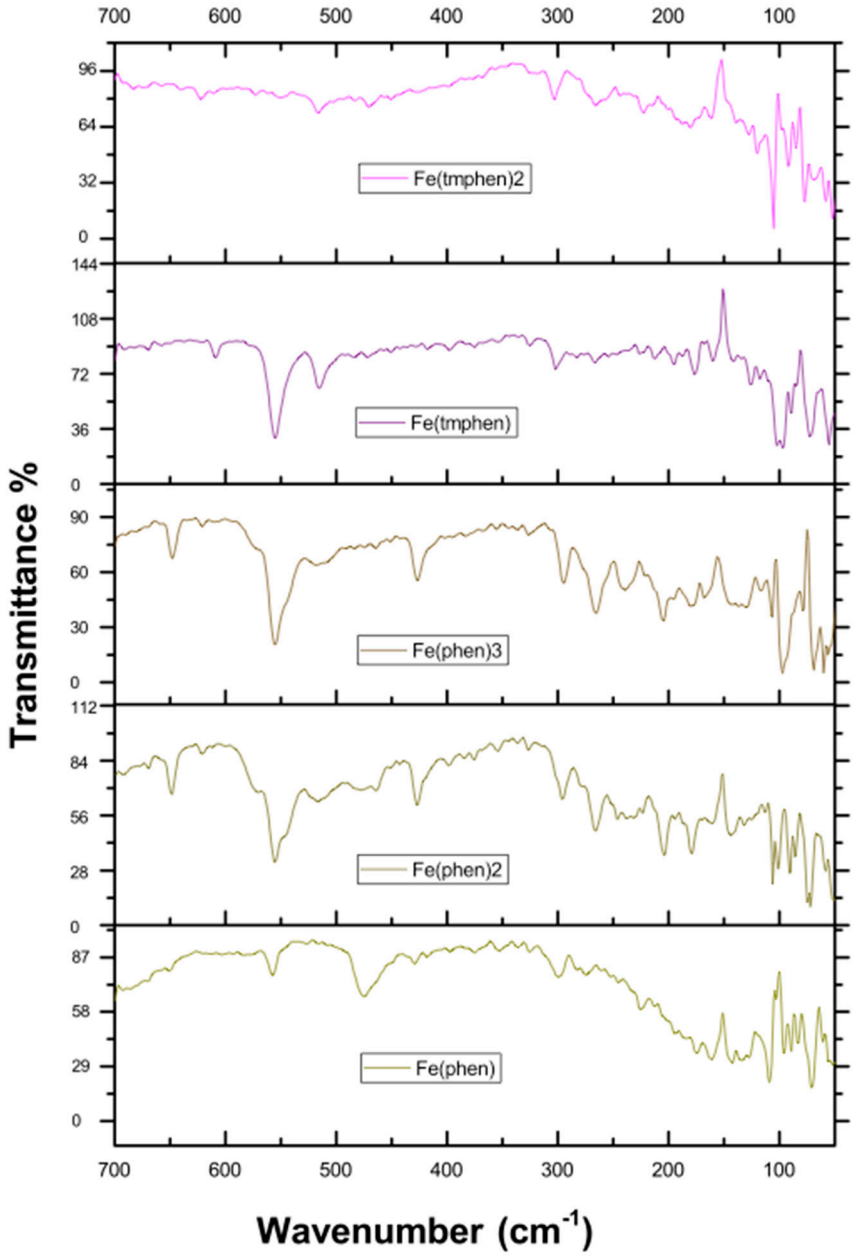

Figure S19. Far infrared spectra of the different Fe(III) complexes with 1,10-phenanthroline or 3,4,7,8-tetramethyl-1,10-phenanthroline.

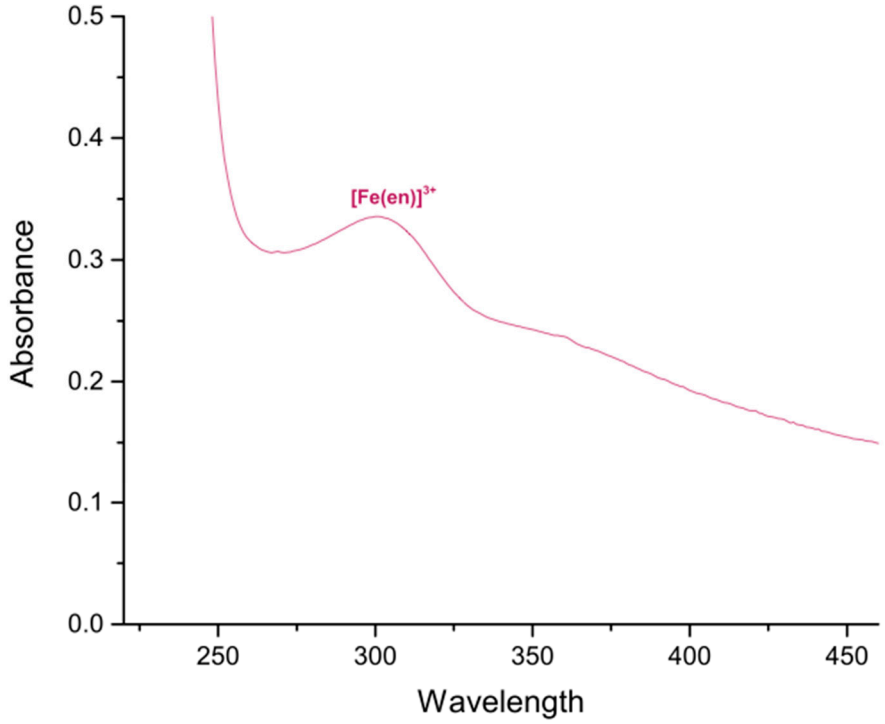

Figure S20. UV-vis spectra of $[Fe(en)]^{3+}$ complex in methanol solution.

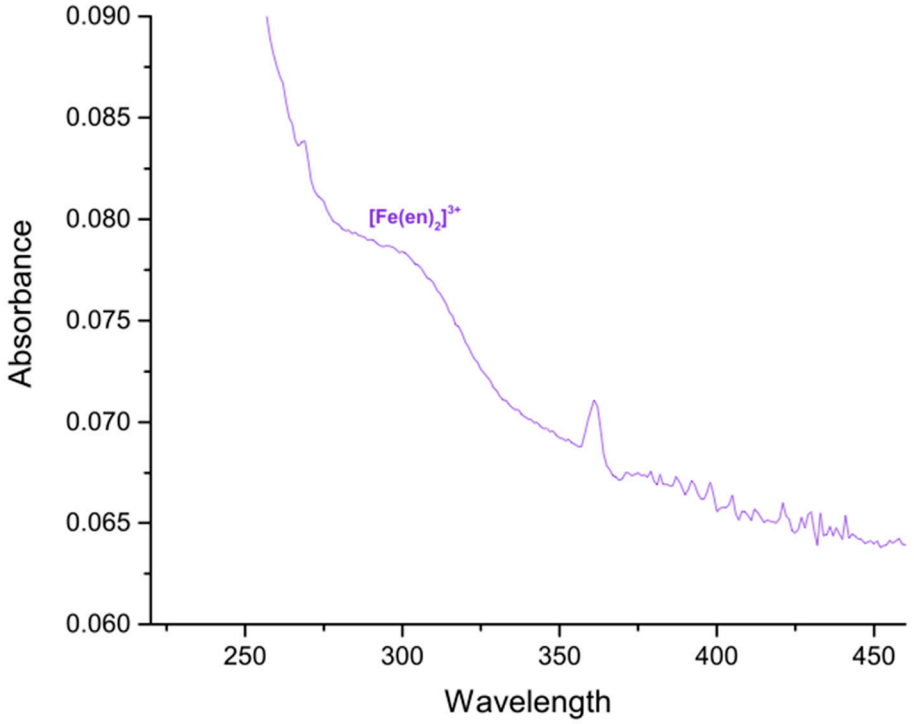

Figure S21. UV-vis spectrum of $[Fe(en)_2]^{3+}$ complex in methanol solution.

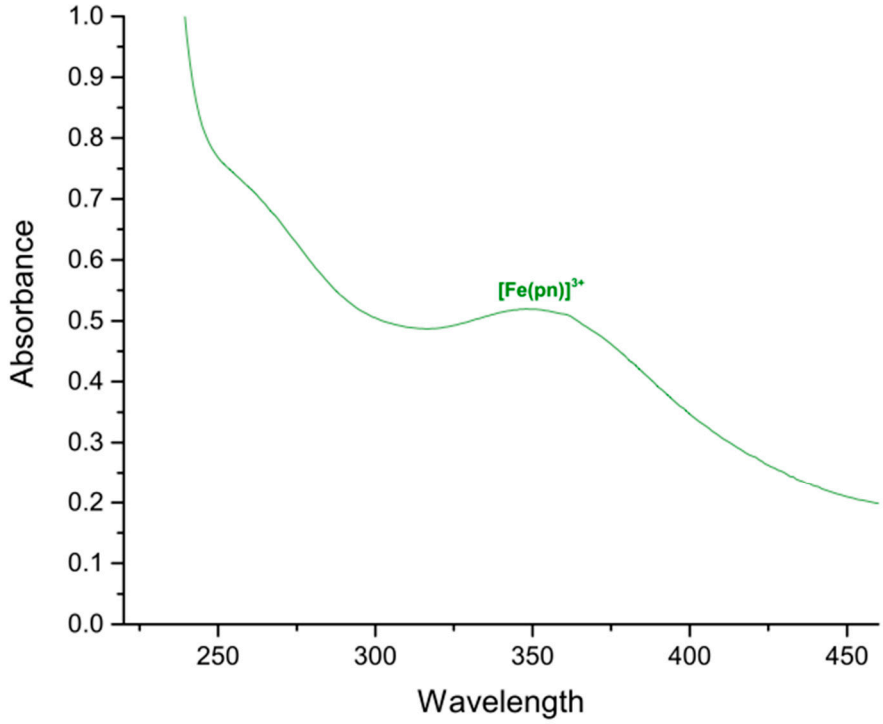

Figure S22. UV-vis spectrum of $[Fe(pn)]^{3+}$ complex in methanol solution.

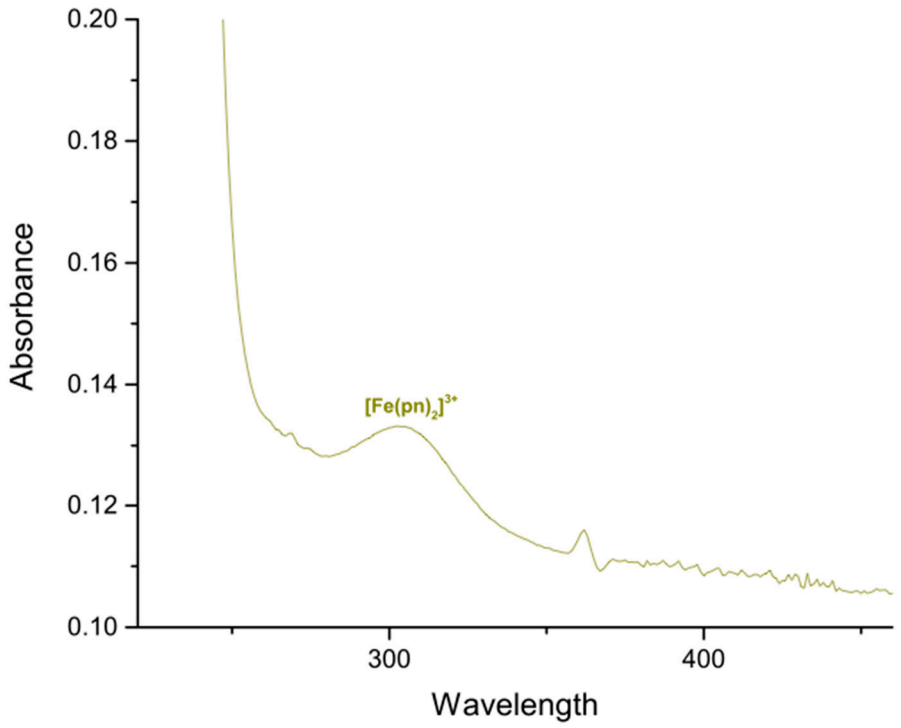

Figure S23. UV-vis spectrum of $[Fe(pn)_2]^{3+}$ complex in methanol solution.

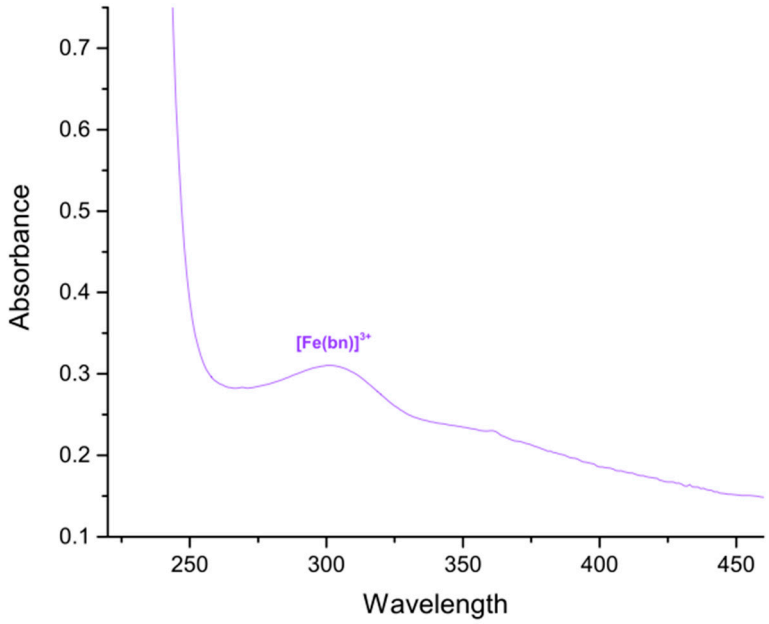

Figure S24. UV-vis spectrum of $[Fe(bn)]^{3+}$ complex in methanol solution.

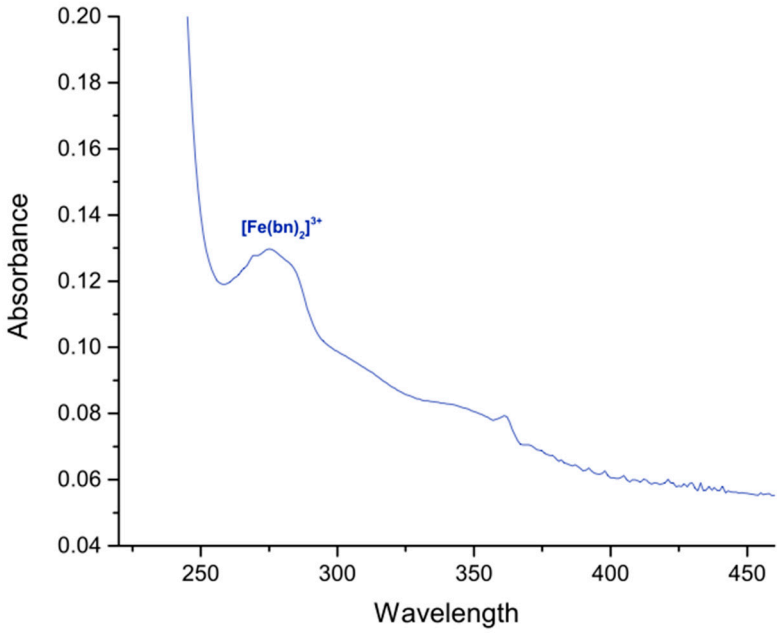

Figure S25. UV-vis spectrum of $[Fe(bn)_2]^{3+}$ complex in methanol solution.

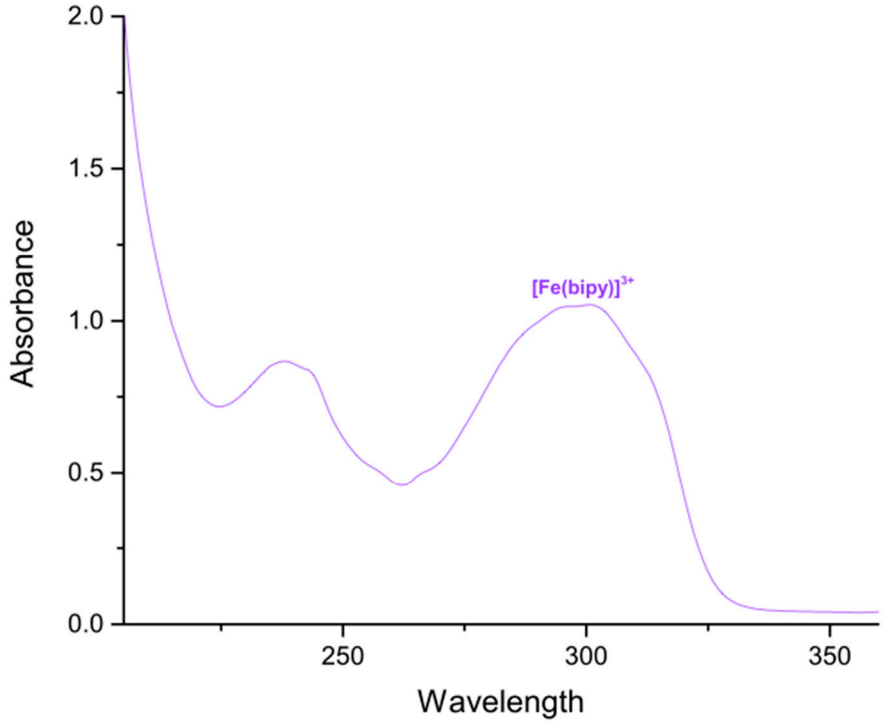

Figure S26. UV-vis spectrum of $[Fe(bipy)]^{3+}$ complex in methanol solution.

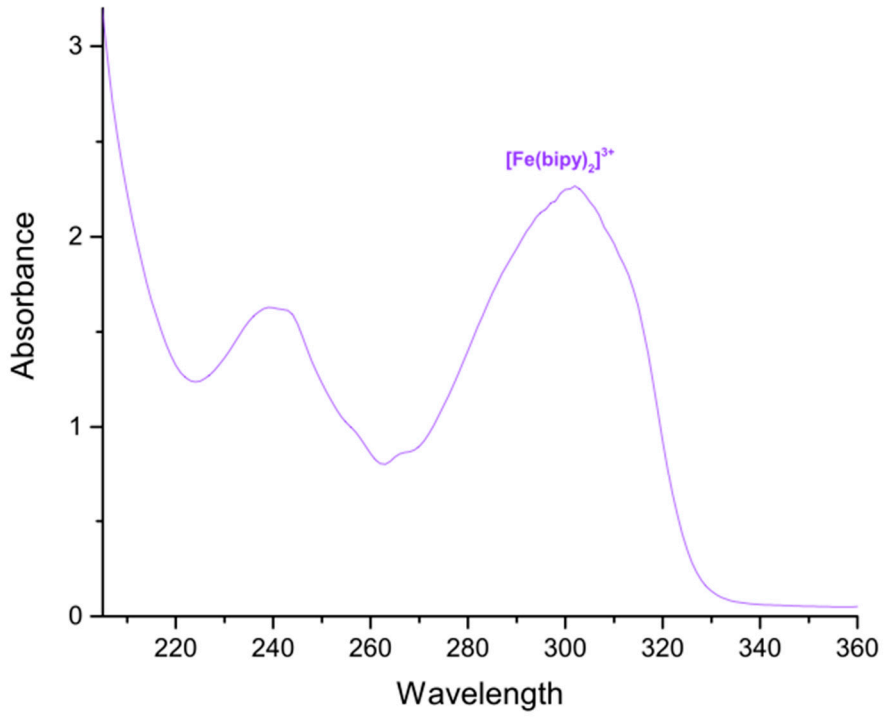

Figure S27. UV-vis spectrum of $[Fe(bipy)_2]^{3+}$ complex in methanol solution.

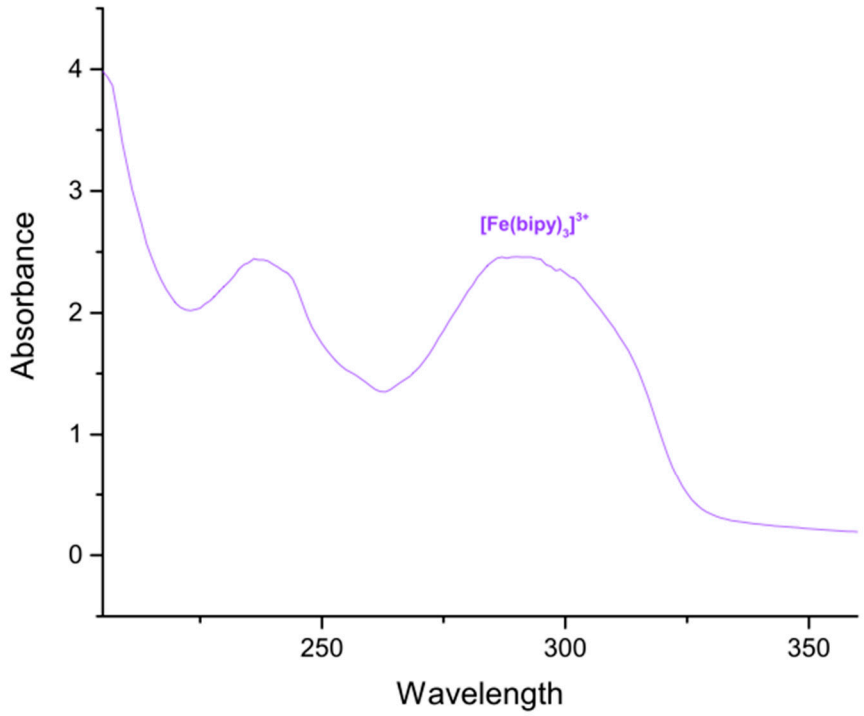

Figure S28. UV-vis spectrum of $[Fe(bipy)_3]^{3+}$ complex in methanol solution.

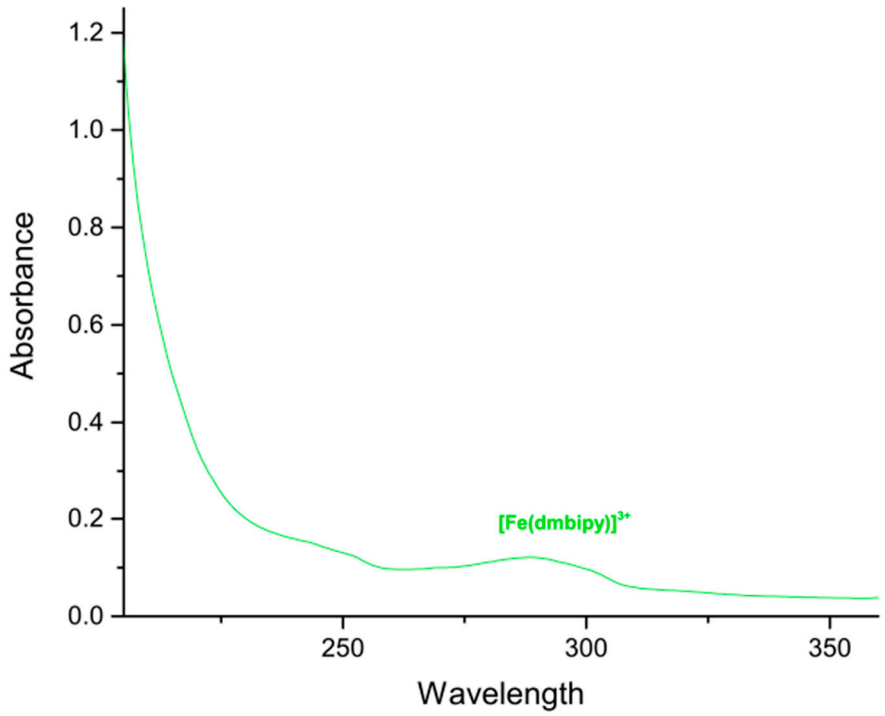

Figure S29. UV-vis spectrum of $[Fe(dmbipy)]^{3+}$ complex in methanol solution.

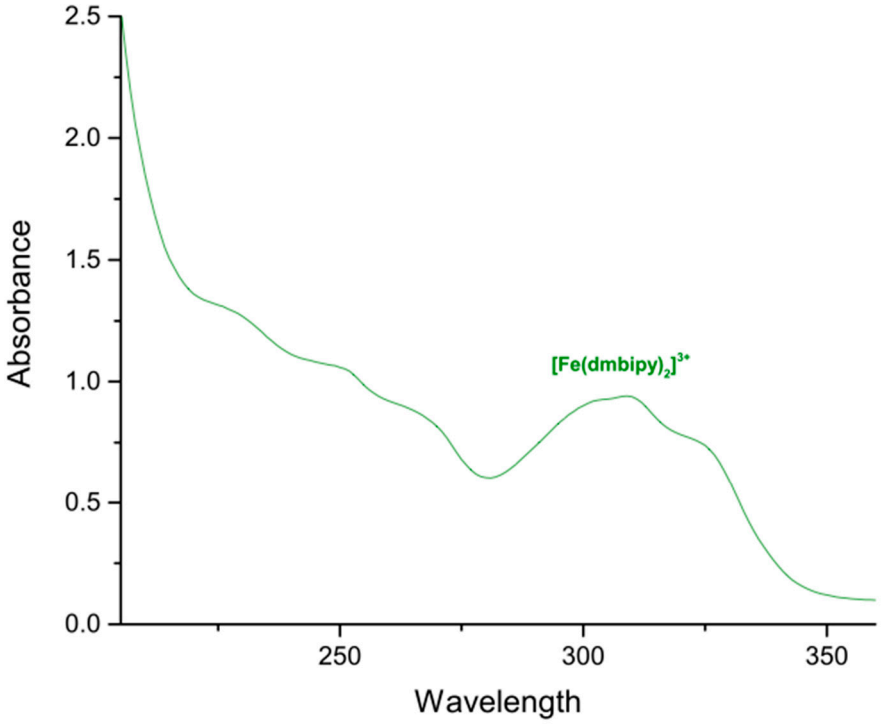

Figure S30. UV-vis spectrum of $[Fe(dmbipy)_2]^{3+}$ complex in methanol solution.

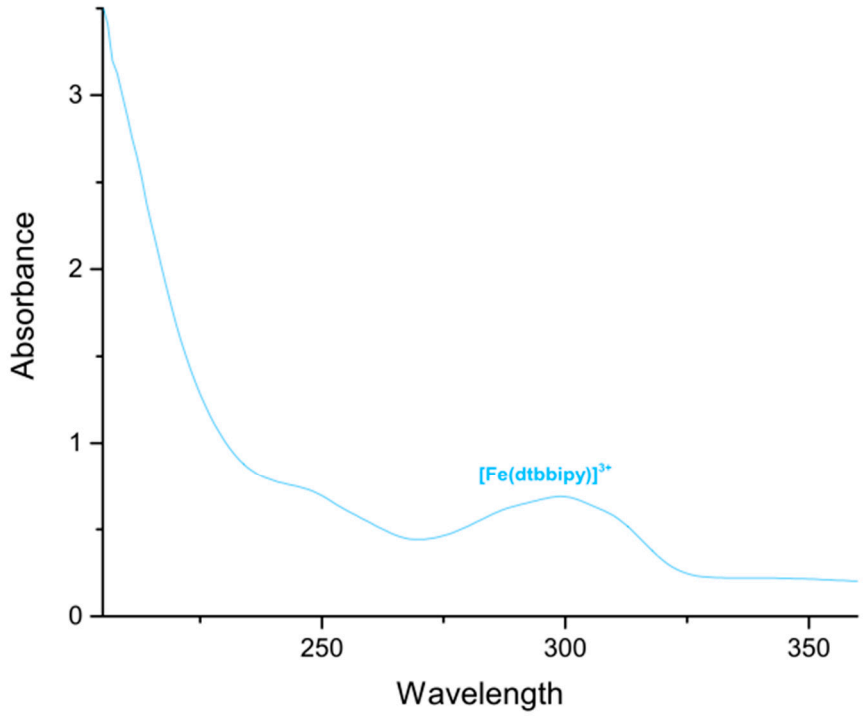

Figure S31. UV-vis spectrum of $[Fe(dtbbipy)]^{3+}$ complex in methanol solution.

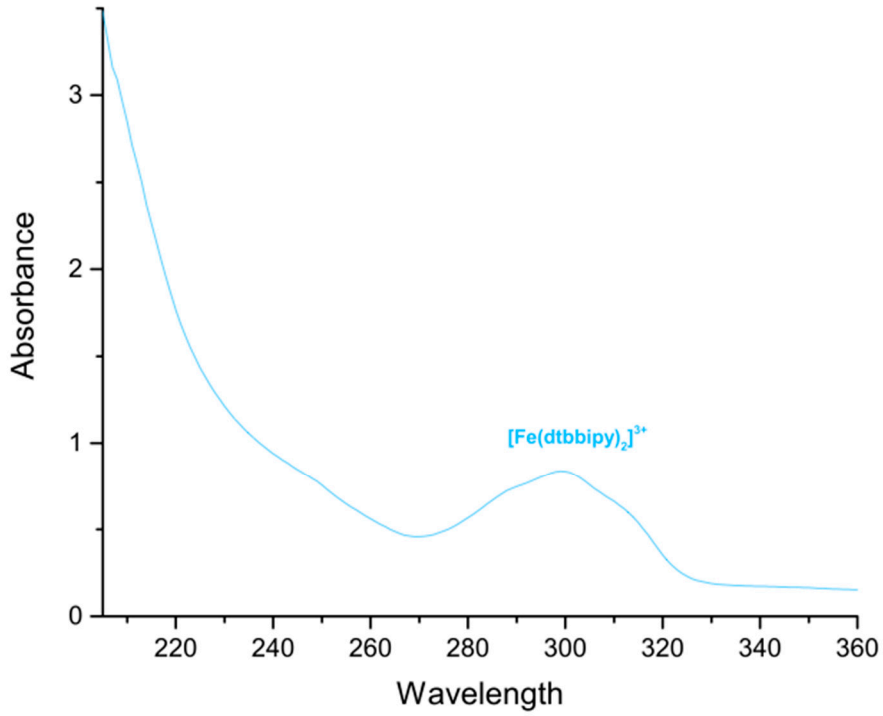

Figure S32. UV-vis spectrum of $[Fe(dtbbipy)_2]^{3+}$ complex in methanol solution.

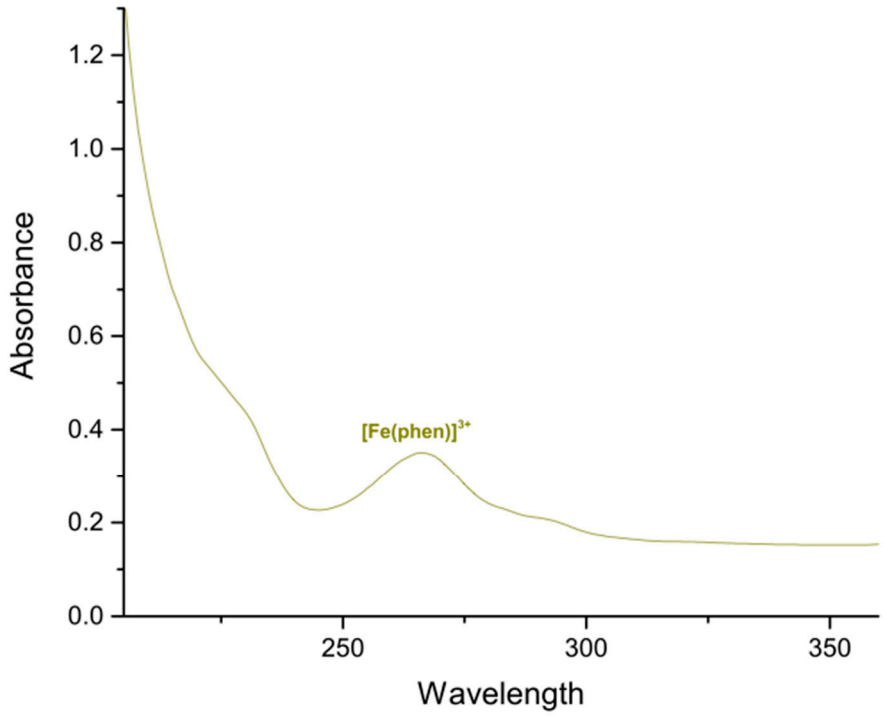

Figure S33. UV-vis spectrum of $[Fe(phen)]^{3+}$ complex in methanol solution.

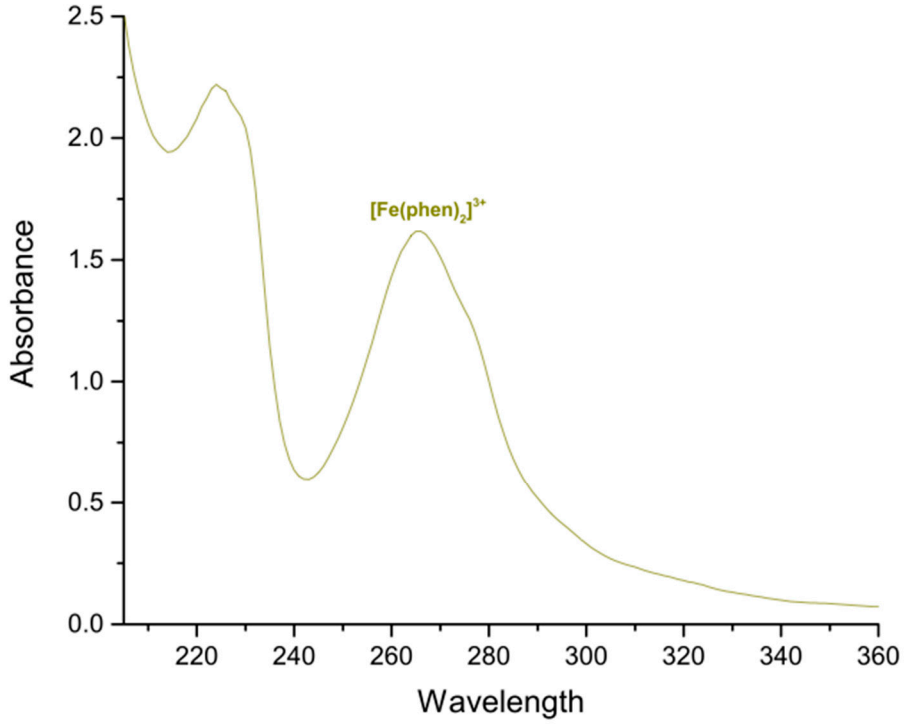

Figure S34. UV-vis spectrum of $[Fe(phen)_2]^{3+}$ complex in methanol solution.

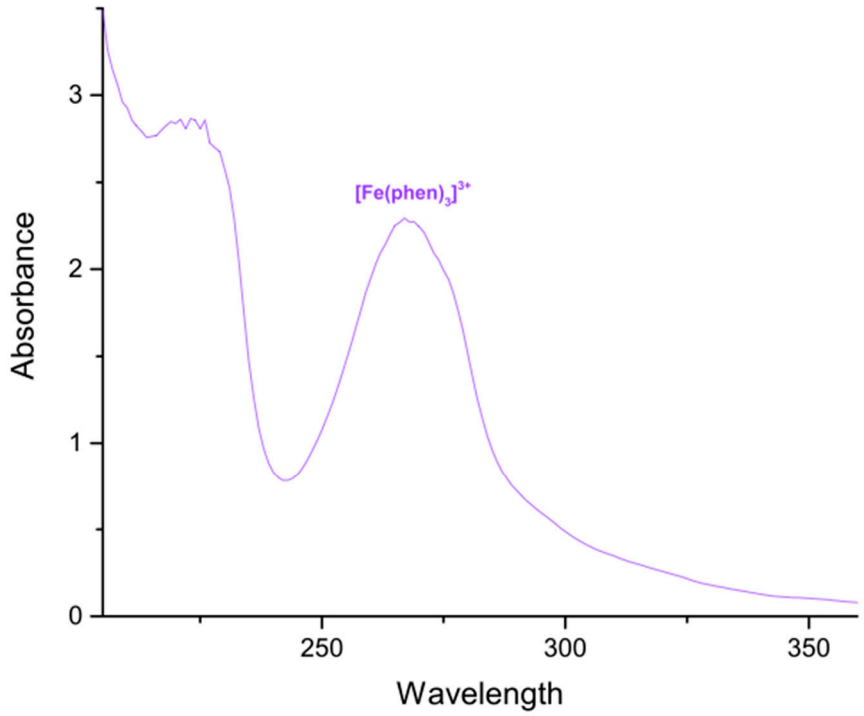

Figure S35. UV-vis spectrum of $[Fe(phen)_3]^{3+}$ complex in methanol solution.

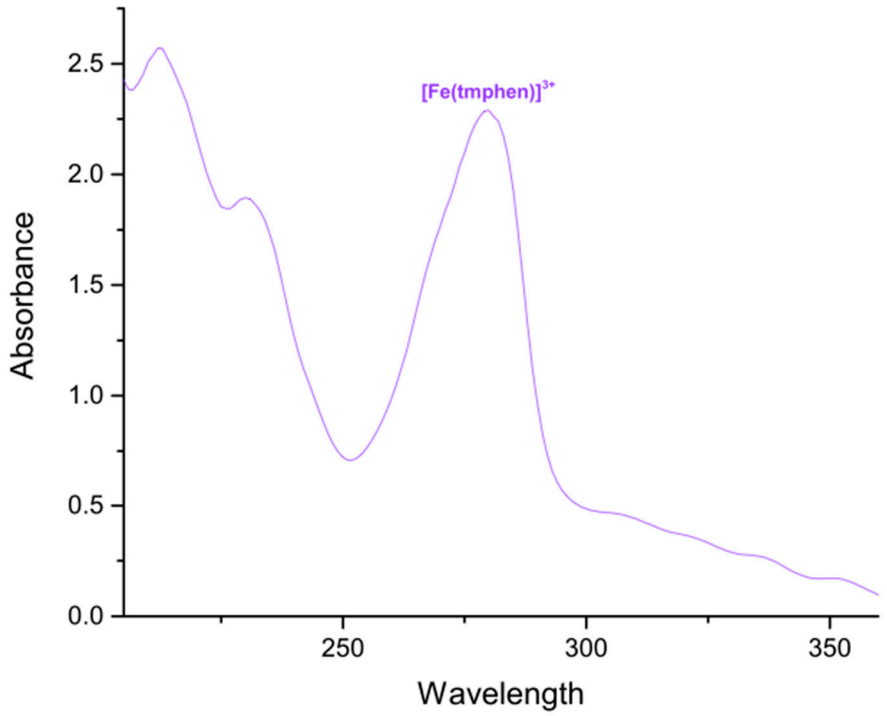

Figure S36. UV-vis spectrum of $[Fe(tmphen)]^{3+}$ complex in methanol solution.

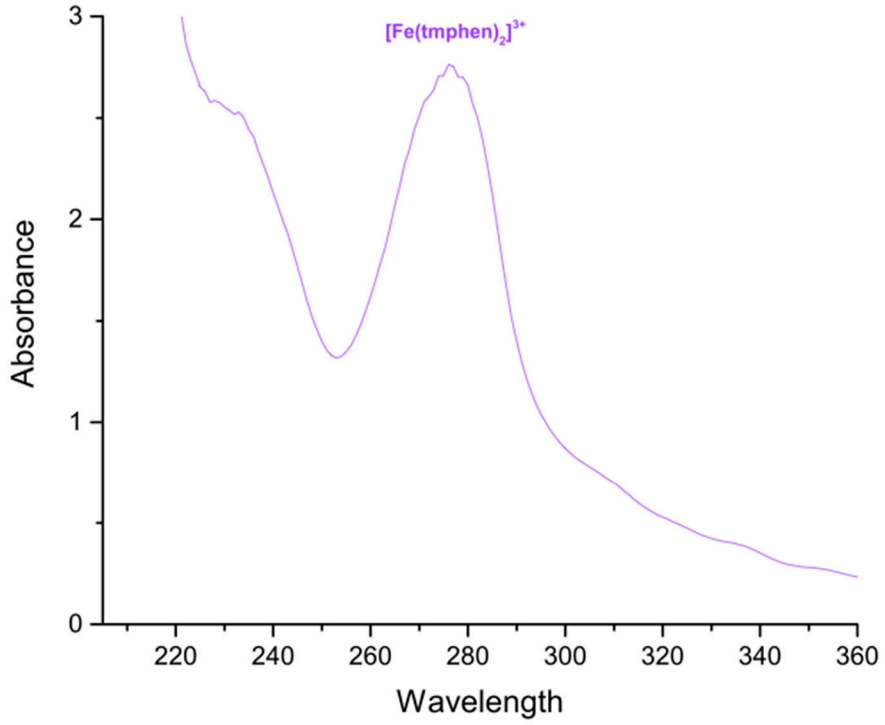

Figure S37. UV-vis spectrum of $[Fe(tmphen)_2]^{3+}$ complex in methanol solution.