Electronic Supplementary Material (ESI) for Dalton Transactions

Pyochelin, a siderophore of *Pseudomonas aeruginosa* : Physicochemical characterization of the iron(III), copper(II) and zinc(II) complexes

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Supporting Information Available

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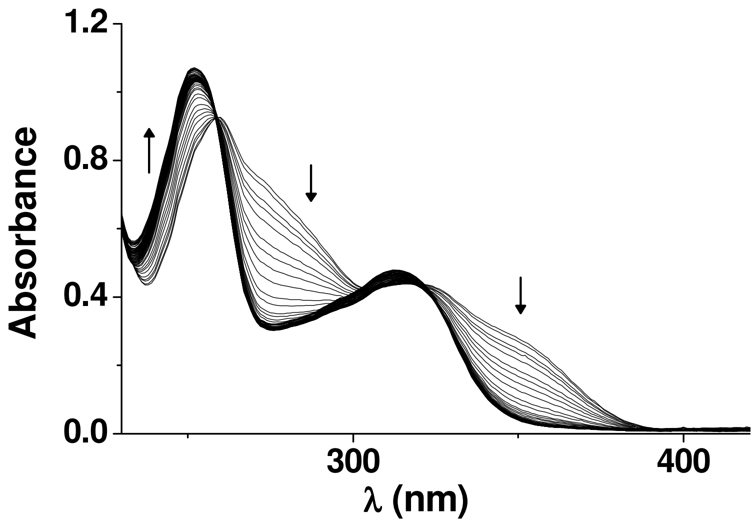
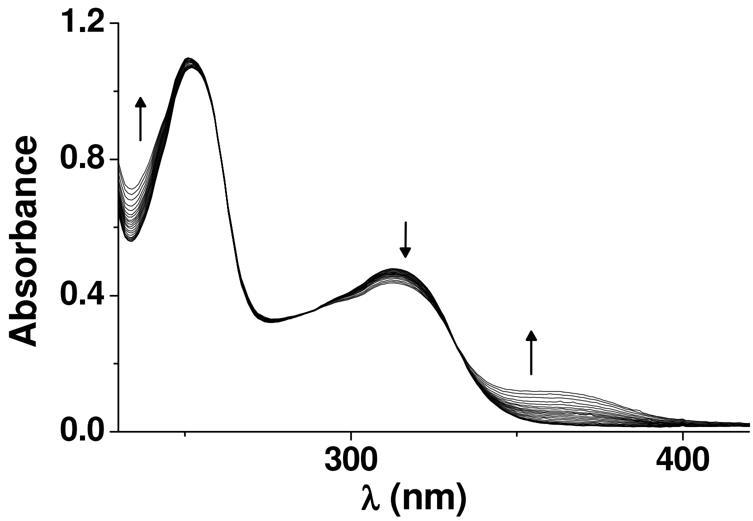


(a)



(b)

Figure S1. Spectrophotometric versus p[H] titration of pyochelin. Solvent: CH_3OH/H_2O (80/20 by weight); I = 0.1 M (($(C_2H_5)NClO_4$); T = 25.0(2) °C; ℓ = 1 cm; $[\mathbf{L}]_{tot}$ = 1.03×10^{-4} M; a) 2.54 < p[H] < 9.24; b) 9.24 < p[H] < 12.10.

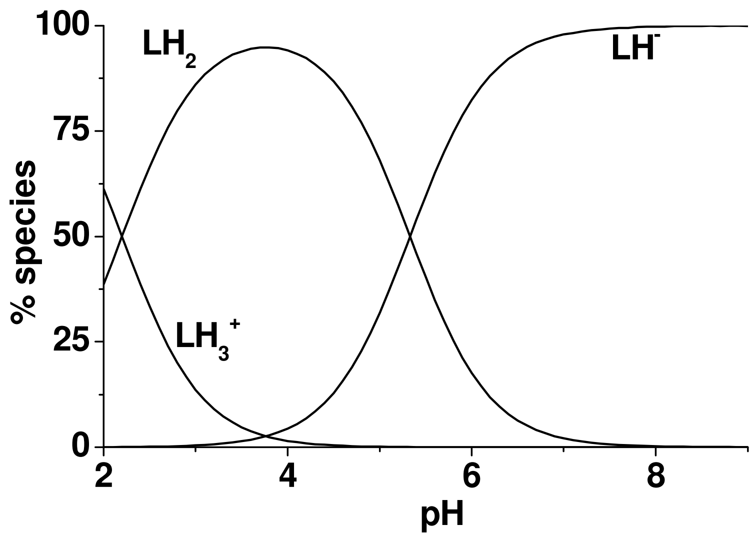


Figure S2. Distribution diagrams of the protonated species of pyochelin. $[\mathbf{L}]_{tot} = 1.03 \times 10^{-4}$ M; solvent: CH_3OH/H_2O (80/20 by weight); I = 0.1 M ($(C_2H_5)_4NClO_4$); T = 25.0(2) °C.

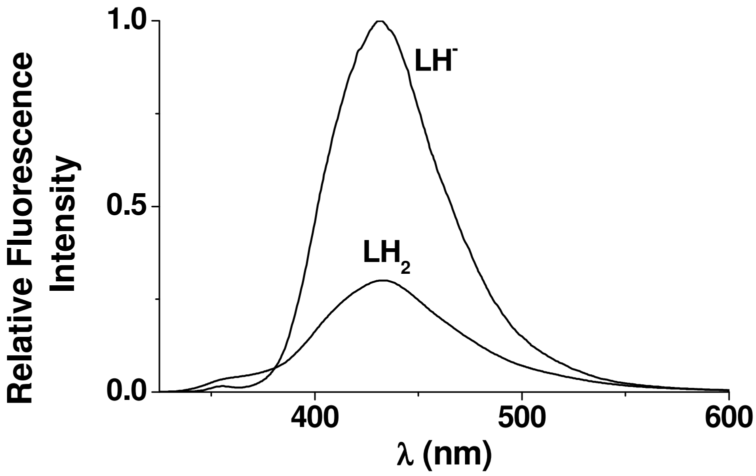


Figure S3. Relative recalculated emission spectra of the protonated species of pyochelin. Solvent: CH_3OH/H_2O (80/20 by weight); I = 0.1 M ($(C_2H_5)_4NClO_4$); T = 25.0(2) °C. $\mathbf{LH_3}^+$ is considered as a not emitting species.

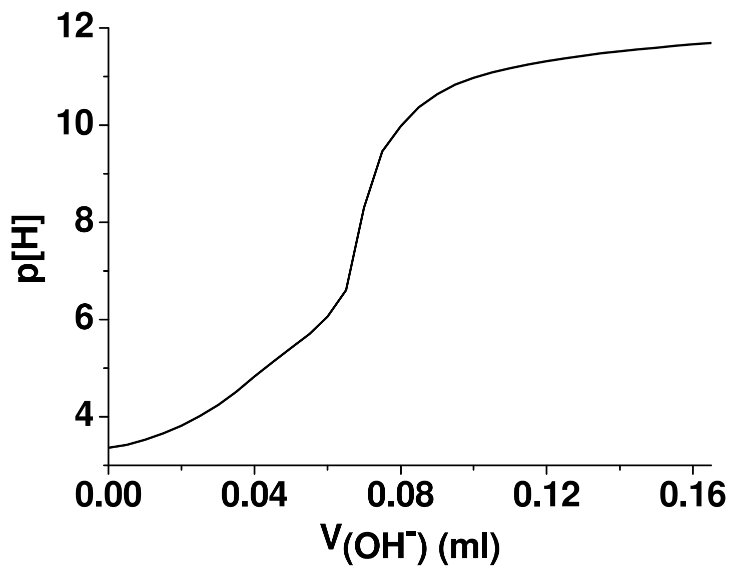
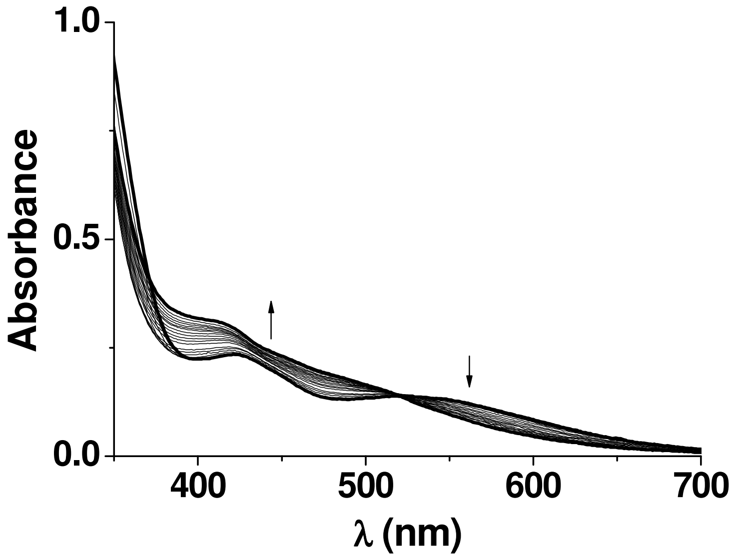
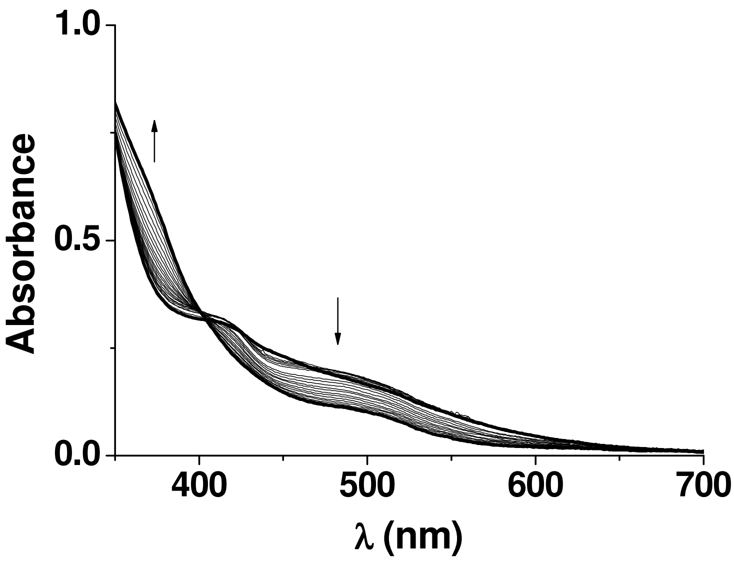


Figure S4. Potentiometric titration curve of pyochelin Fe(III) complexes. [**L**]$_{tot}$ = 1.50 × 10^{-3} M; [Fe(III)]$_{tot}$/[**L**]$_{tot}$ = 0.21; 3.36 < p[H] < 11.69; solvent: CH_3OH/H_2O (80/20 by weight); T = 25.0(2) °C; I = 0.1 M ($(C_2H_5)_4NClO_4$).

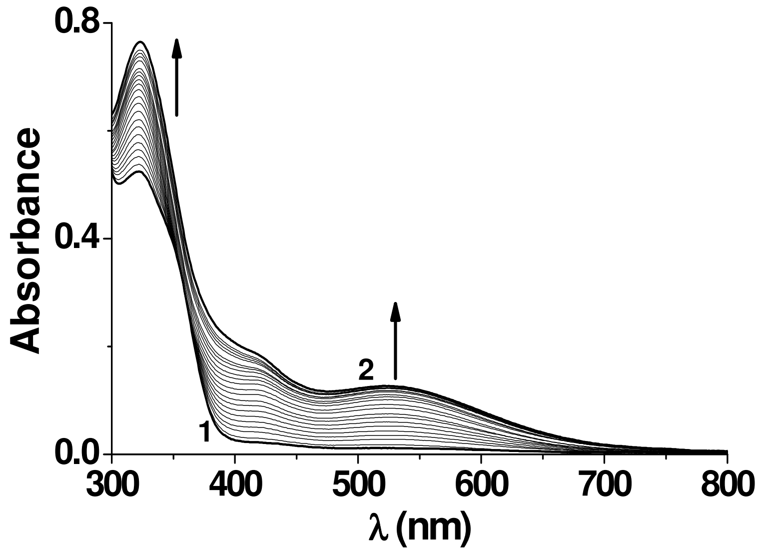


(a)



(b)

Figure S5. Spectrophotometric titration of the pyochelin Fe(III) complexes from a) 2.45 < p[H] < 7.63 and from b) 7.63 < p[H] < 11.43. $[\mathbf{L}]_{tot}$ = 3.36 × 10^{-4} M; $[\mathbf{L}]_{tot}$ /$[Fe(III)]_{tot}$ = 4.0; solvent: CH_3OH/H_2O (80/20 by weight); T = 25.0 (2) °C; I = 0.1 M ($(C_2H_5)_4NClO_4$); ℓ = 1 cm.



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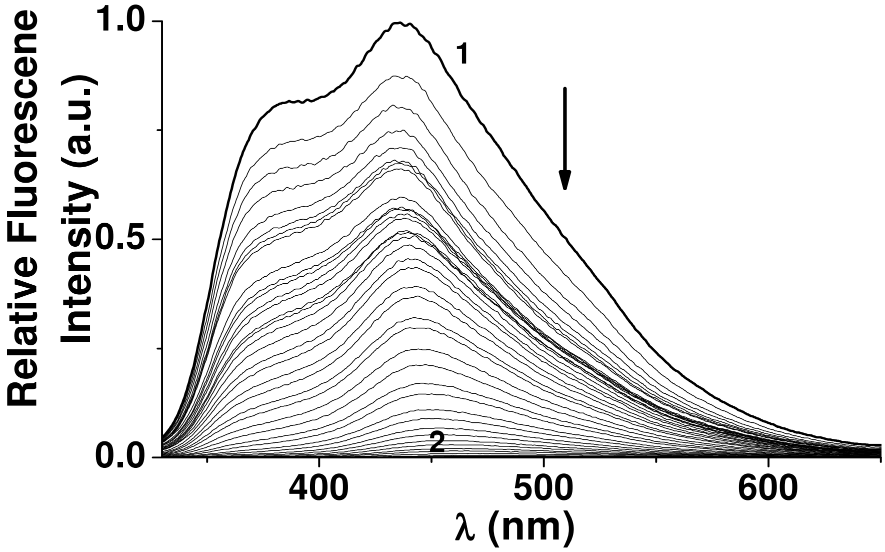


(b)

Figure S6. Spectrophotometric (absorption (a) and emission (b)) titrations of pyochelin by iron(III) at pH 2. (a) 1) $[\mathbf{L}]_{tot} = 1.13 \times 10^{-4}$ M; 2) $[Fe(III)]_{tot} / [\mathbf{L}]_{tot} = 1.1$. (b) 1) $[\mathbf{L}]_{tot} = 2.02 \times 10^{-5}$ M; 2) $[Fe(III)]_{tot}/ [\mathbf{L}]_{tot} = 111.8$; $\lambda_{exc} = 322$ nm. Solvent: CH_3OH/H_2O (80/20 by weight)); $I = 0.1$ M ($(C_2H_5)_4NClO_4$); $T = 25.0(2)$ °C; $\ell = 1$ cm.

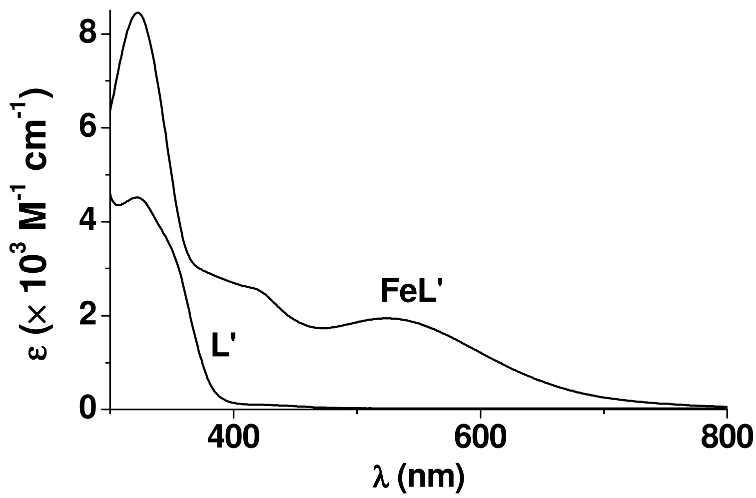


Figure S7. Electronic spectra of the pyochelin ferric monochelate complex at p[H] 2. Solvent: CH_3OH/H_2O (80/20 by weight); I = 0.1 M ($(C_2H_5)_4NClO_4$); T = 25.0(2) °C. **L'** designates the protonated pyochelin species at p[H] 2.0.

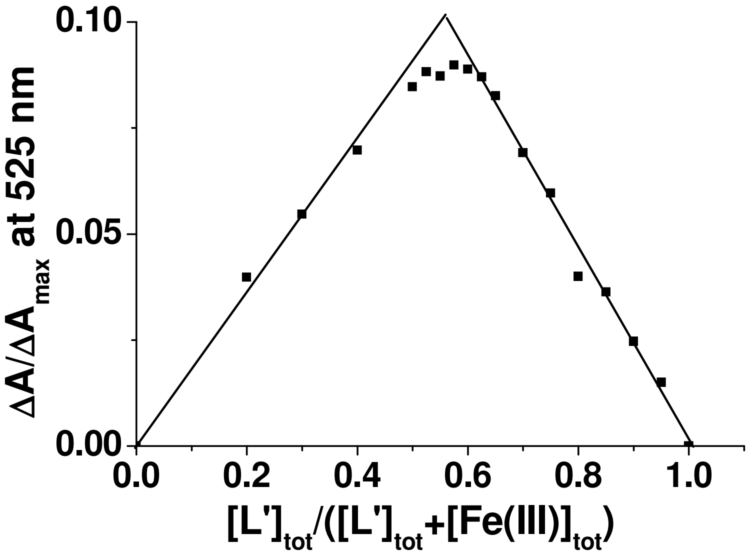


Figure S8. Job's plot ($\Delta A/\Delta A_{max}$ at 525 nm) upon mixing **L'** and Fe(III) at p[H] 2.0. ([**L'**]$_{tot}$ + [Fe(III)]$_{tot}$) = 9.95×10^{-5} M; solvent: MeOH/H_2O (80/20 by weight); I = 0.1 M ($N(C_2H_5)_4ClO_4$); T = 25.0(2) °C; ℓ = 1 cm. **L'** designates the protonated pyochelin species at p[H] 2.0.

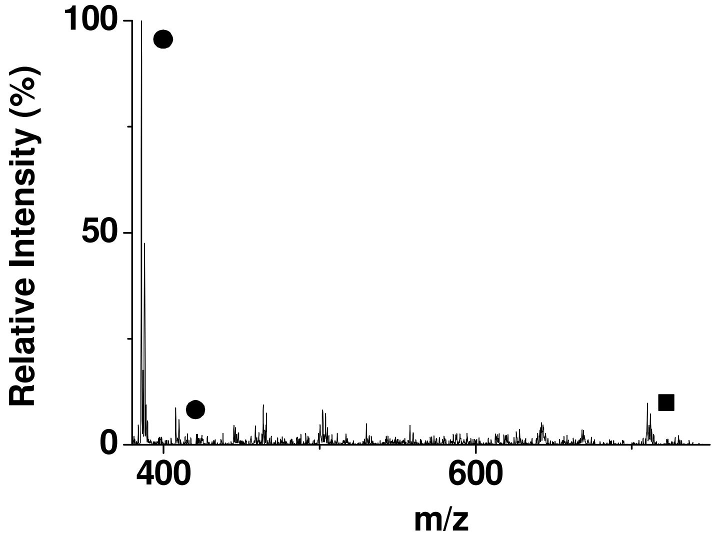
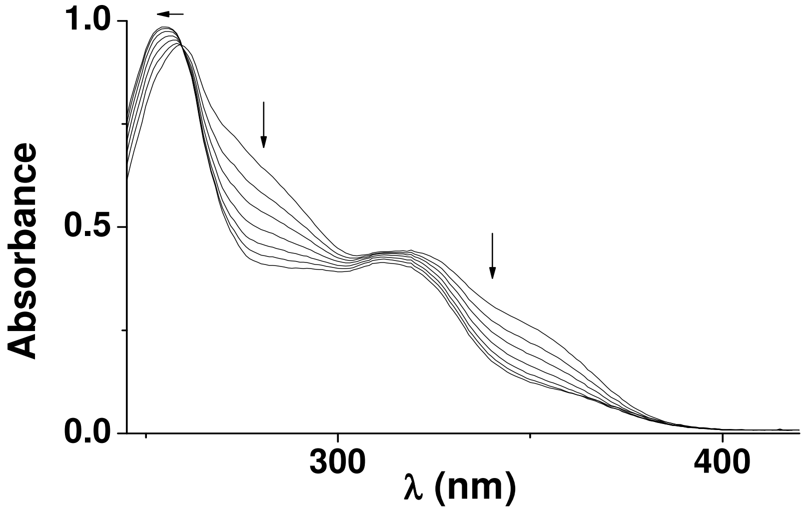
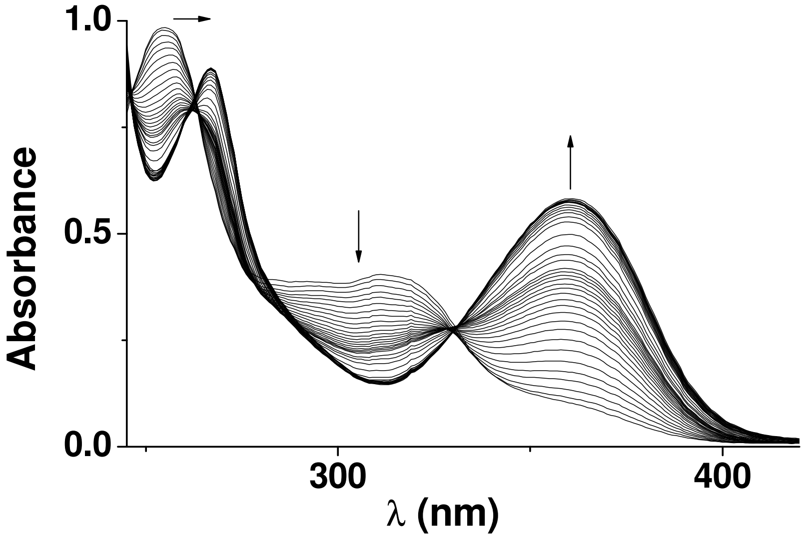


Figure S9. ESI-MS spectra of the Cu(II) complexes of pyochelin. $[\mathbf{L}]_{tot} = 1.95 \times 10^{-5}$ M; $[Cu(II)]_{tot}/[\mathbf{L}]_{tot} = 0.49$; solvent: CH_3OH/H_2O (80/20 by weight); p[H] ~ 4-5; positive mode. Cu**L** (●), Cu$\mathbf{L}_2$ (■). **L** designates the fully deprotonated ligand.

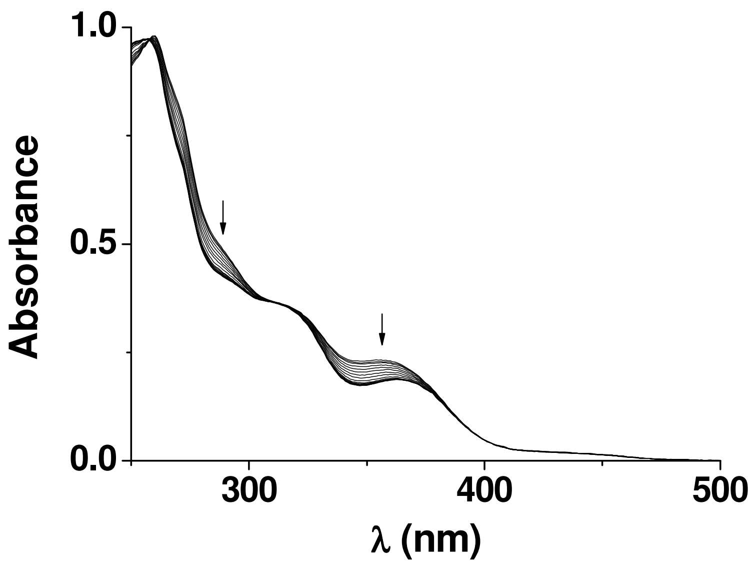


(a)



(b)

Figure S10. Spectrophotometric titration versus p[H] of pyochelin Zn(II) complexes. $[\mathbf{L}]_{tot} = 9.68 \times 10^{-5}$ M; $[Zn(II)]_{tot}/[\mathbf{L}]_{tot} = 1.0$; a) $2.34 < p[H] < 3.4$; b) $3.4 < p[H] < 10.26$; solvent: CH_3OH/H_2O (80/20 by weight); $T = 25(2)$ °C; $I = 0.1$ M ($(C_2H_5)_4NClO_4$); $l = 1$ cm.



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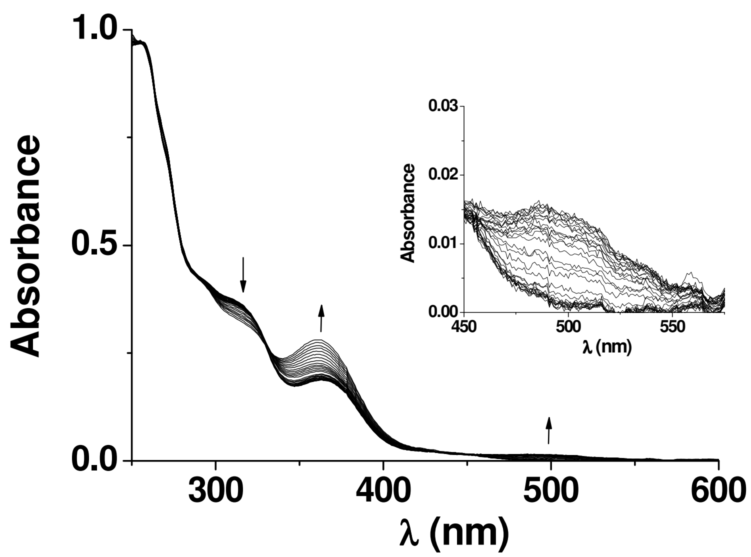
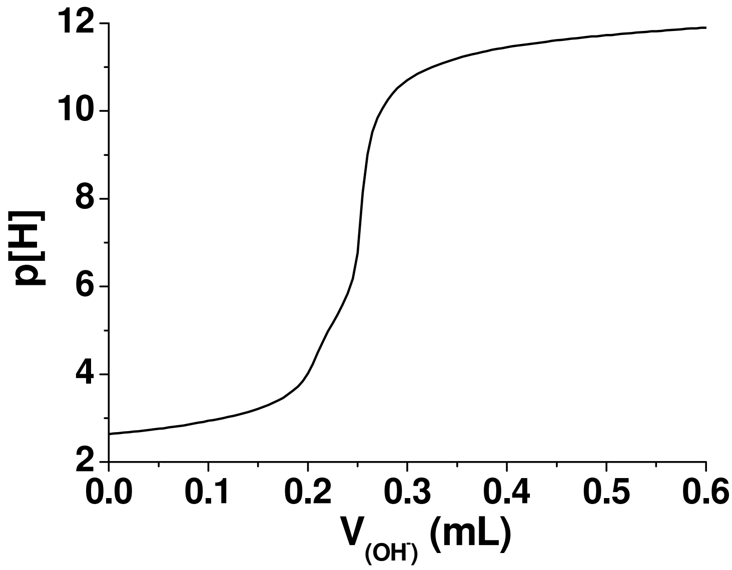
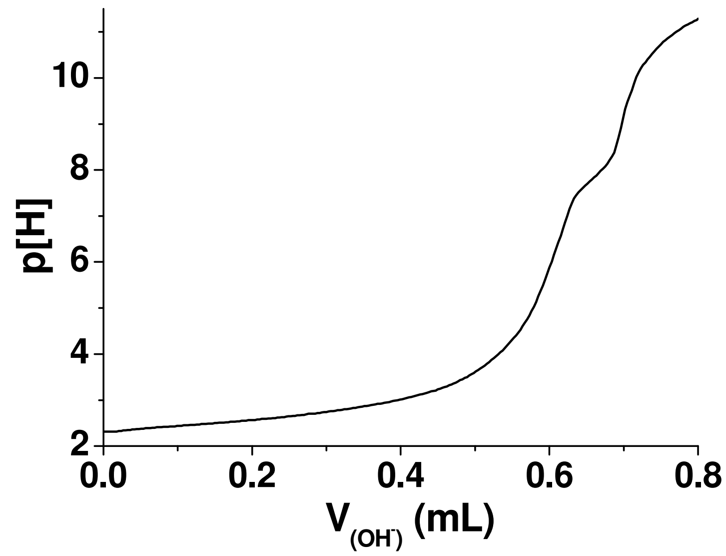


(b)

Figure S11. Spectrophotometric titration versus p[H] of the pyochelin cupric complexes. $[\mathbf{L}]_{tot} = 9.22 \times 10^{-5}$ M; $[Cu(II)]_{tot}/[\mathbf{L}]_{tot} = 0.33$; a) 2.68 < p[H] < 4.4; b) 4.4 < p[H] < 11.48; solvent: CH_3OH/H_2O (80/20 by weight); $T = 25.0(2)$ °C; $I = 0.1$ M $((C_2H_5)_4NClO_4)$; $l = 1$ cm.



(a)



(b)

Figure S12. Potentiometric titration of a) pyochelin Cu(II) and b) pyochelin Zn(II) complexes. a) $[\mathbf{L}]_{tot} = 1.13 \times 10^{-3}$ M, $[Cu(II)]_{tot}/[\mathbf{L}]_{tot} = 0.50$; $2.64 < p[H] < 11.89$. b) $[\mathbf{L}]_{tot} = 1.49 \times 10^{-3}$ M, $[Zn(II)]_{tot}/[\mathbf{L}]_{tot} = 0.50$; $2.32 < p[H] < 11.28$. Solvent: CH_3OH/H_2O (80/20 by weight); $I = 0.1$ M ($(C_2H_5)_4NClO_4$); $T = 25.0(2)$ °C.

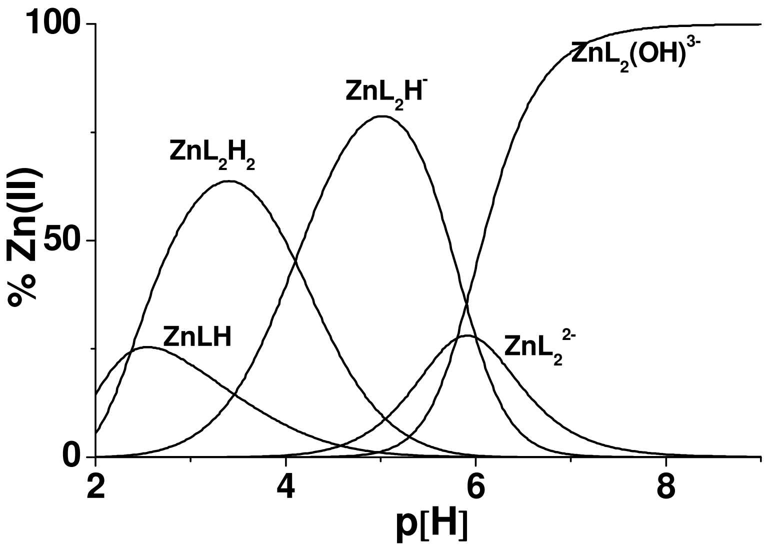


Figure S13. Distribution diagrams of the Zn(II) complexes of pyochelin as a function of p[H]. Solvent: CH_3OH/H_2O (80/20 by weight); I = 0.1 M (($(C_2H_5)_4NClO_4$); T = 25(2) °C; $[Zn(II)]_{tot}/[\mathbf{L}]_{tot} = 0.5$, $[\mathbf{L}]_{tot} = 1.49 \times 10^{-3}$ M.

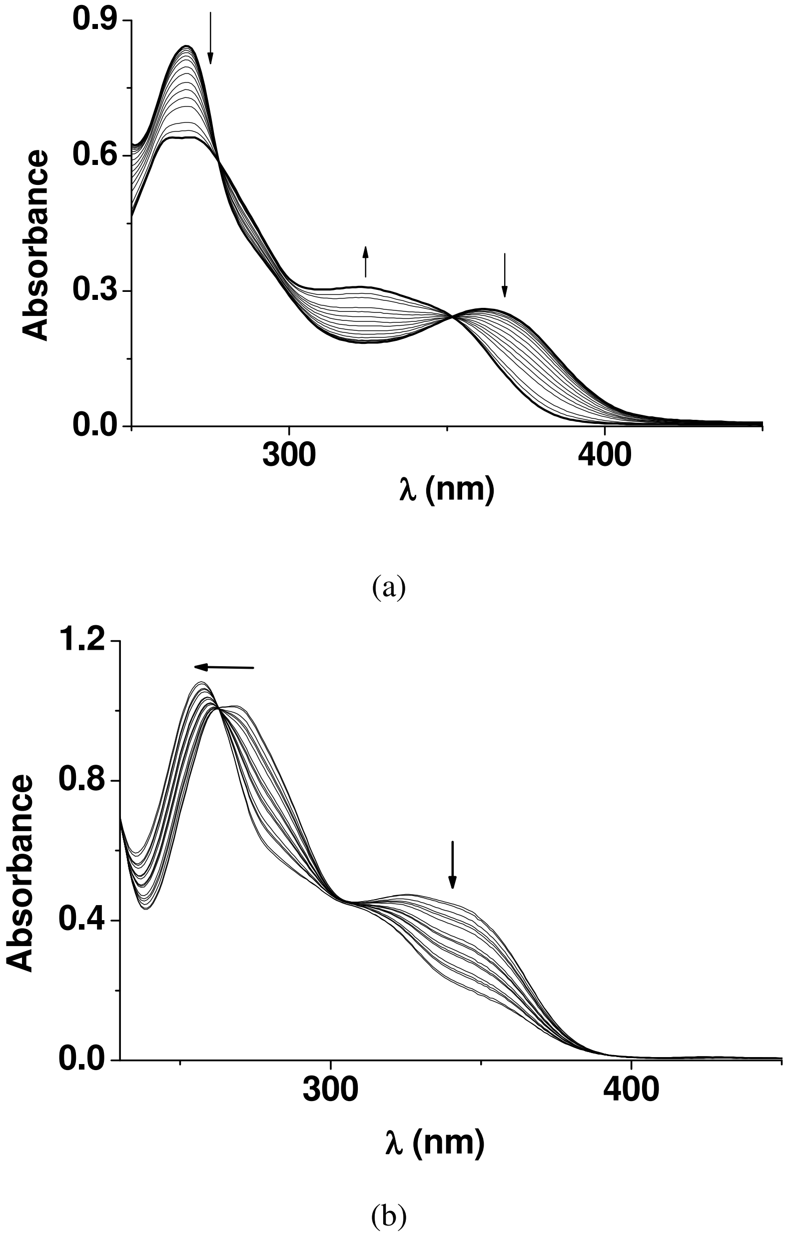
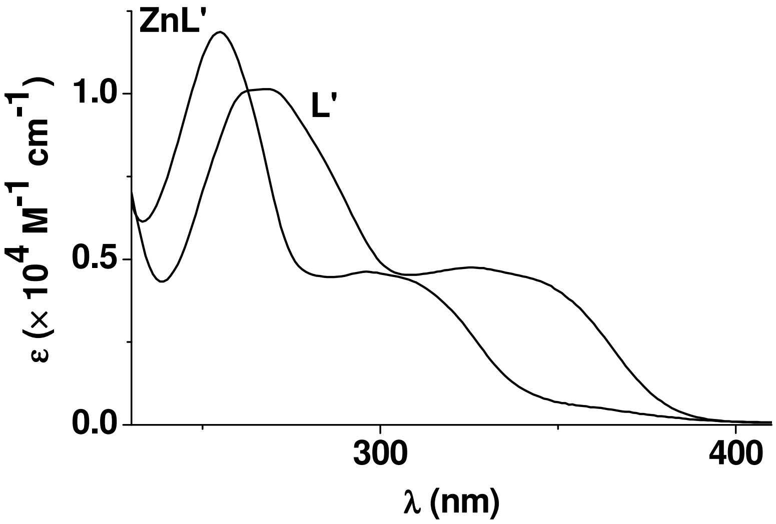
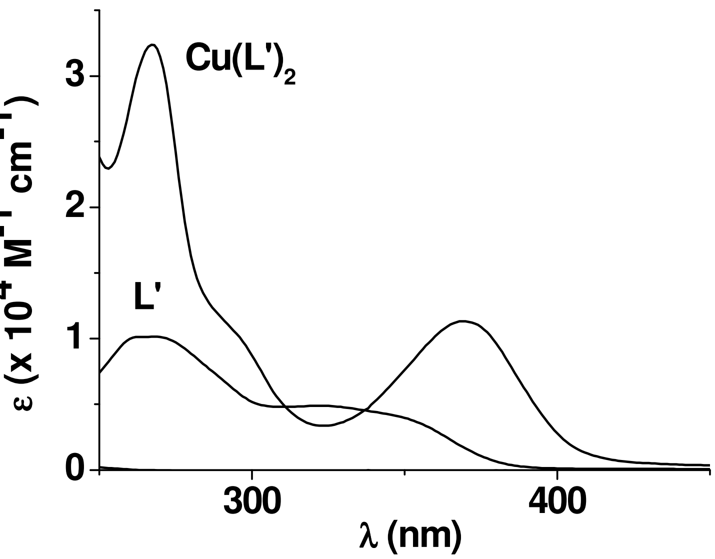


Figure S14. Spectrophotometric titrations of pyochelin versus $[M]_{tot}$ ((a) M = Cu(II), (b) M = Zn(II)) at p[H] 2.0. a) $[\mathbf{L'}]_{tot} = 6.32 \times 10^{-5}$ M; $[Cu(II)]_{tot}/[\mathbf{L'}]_{tot} = 0.69$, $l = 1$ cm. b) $[\mathbf{L'}]_{tot} = 1.0 \times 10^{-4}$ M; $[Zn(II)]_{tot}/[\mathbf{L'}]_{tot} = 191.1$; l = 1cm. Solvent: CH_3OH/H_2O (80/20 by weight); I = 0.1 M ($(C_2H_5)_4NClO_4$); T = 25.0 (2) °C. **L'** designates the protonated pyochelin species at p[H] 2.0.



(a)



(b)

Figure S15. Electronic spectra of a) the Zn(II) pyochelin complexes and of b) the cupric pyochelin complexes at p[H] 2. Solvent: CH_3OH/H_2O (80/20 by weight); $[HClO_4]_{tot}$ = 0.01 M; I = 0.1 M ($(C_2H_5)_4NClO_4$); T = 25.0(2) °C. **L'** designates the protonated pyochelin species at p[H] 2.0.

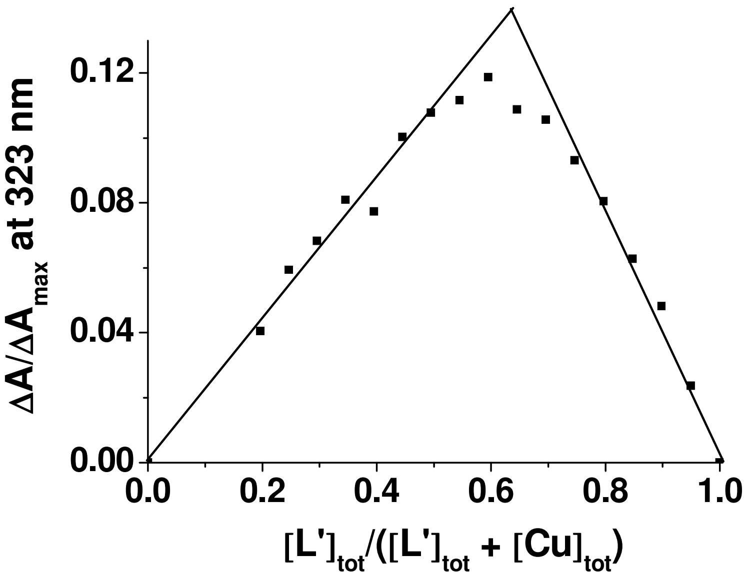
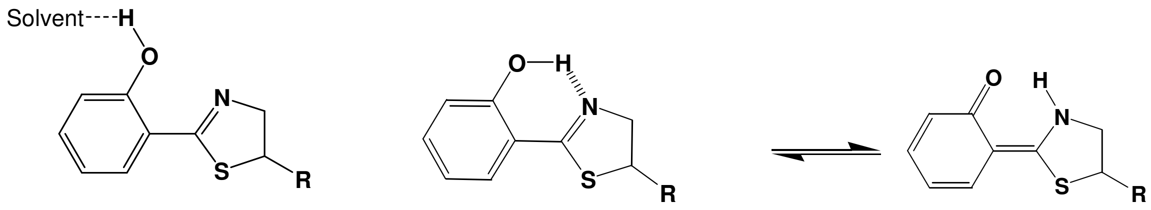


Figure S16. Job's plot ($\Delta A/\Delta A_{max}$ at 323 nm) upon mixing **L'** and Cu(II) at p[H] 2.0. ($[\mathbf{L'}]_{tot}$ + $[Cu(II)]_{tot}$) = 2.0×10^{-4} M; solvent: MeOH/H_2O (80/20 by weight); I = 0.1 M ($N(C_2H_5)_4ClO_4$); T = 25.0(2) °C, ℓ = 1 cm. **L'** designates the protonated pyochelin species at p[H] 2.0.



Cis-Open Enol	Cis-Closed Enol	Ketone form
(noted *cis*-O)	(noted cis-C)	(noted K)

Figure S17. Possible conformers and tautomers of pyochelin in solution.

Pseudomolecular Ions	m/z experimental	m/z simulated
[**L** + Fe]$^+$	377.8	377.2
[**L** + Fe + H_2O]$^+$	395.9	396.3
[**L** + Fe + ClO_4 + Na]$^+$	499.9	499.9
[2**L** + Fe + 2H]$^+$	701.9	702.0
[**L** + Cu + H]$^+$	385.9	386.0
[**L** + Cu + Na]$^+$	407.9	408.0
[2**L** + Cu + 3H]$^+$	709.9	710.0
[**L** + Zn + H]$^+$	381.0	380.9
[2**L** + Zn + 3H]$^+$	705.0	704.9

Table S1. Intensity maxima of the major pyochelin metal complexes (Fe(III), Cu(II), Zn(II)) observed by ESI-MS. Solvent: CH_3OH/H_2O (80/20 by weight); p[H] ~4-5; positive mode. **L** designates the fully deprotonated ligand.

$[Fe(III)]_{tot}$ ($\times 10^{-3}$ M)	($k_{obs} \pm 3\sigma$) (s^{-1}) $[H^+]_{tot} \times 10^{-3}$ (M)						
	3.09	5.01	7.76	12.59	19.95	31.6	50.12
0.26	0.53(9)	0.53(5)	0.43(3)	0.34(4)	0.25(2)	0.14(1)	0.14(1)
0.43	0.8(1)	0.9(1)	0.58(6)	0.48(4)	0.31(3)	0.20(3)	0.19(2)
0.69	1.3(2)	1.4(2)	0.9(1)	0.74(6)	0.53(5)	0.35(3)	0.25(4)
0.86	1.9(2)	1.8(2)	1.0(1)	0.85(8)	0.72(7)	0.39(4)	0.45(4)
1.30	2.7(5)	2.4(4)	1.8(2)	1.3(2)			
1.73	2.9(5)	2.8(6)	1.8(3)	1.8(3)			
2.16	3.8(7)	3.5(7)	2.4(6)	2.1(4)			

Table S2. Variation of the pseudo-first order rate constants versus the total concentration of iron(III) and proton. Solvent: CH_3OH/H_2O (80/20 by weight); I = 0.1 M ($(C_2H_5)_4NClO_4$); T = 25.0 (2) °C; $[\mathbf{L}]_{tot} = 8.65 \times 10^{-6}$ M.

λ_{max} (nm) ($\varepsilon \times 10^3$ M^{-1} cm^{-1})			
Pyochelin (L)		**HPT**	
L^{2-}	-	HPT^-	358 (4.8) 277 (3.0)
LH^-	313 (4.9) 252 (11.0)	(HPT)H	320 (4.6) 290 (3.6)
LH_2	313 (0.49) 252 (11.0)		
LH_3^+	345 (6.5) 271 (14.0)	$(HPT)H_2^+$	340 (4.6) 300 (4.4)

Table S3. Spectrophotometric data (λ_{max} ($\varepsilon \times 10^3$) [nm (M^{-1} cm^{-1})] of pyochelin (**L**) and HPT protonated species. Solvent: CH_3OH/H_2O (80/20 by weight); I = 0.1 M; T = 25.0(2) °C. The uncertainties on the λ_{max} and $\varepsilon^{\lambda max}$ are 1 nm and 5%, respectively.

	λ_{max} (nm) ($\varepsilon \times 10^4$ M^{-1} cm^{-1})		
	Zn(II)	**Cu(II)**	**Fe(III)**
ML	/	/	422(0.293) 524(0.182)
ML_2H_2	354(0.38) 310 (0.73) 257 (2.03)	440 (0.05) 364 (0.62) 310 (0.78) 261 (2.37)	/
ML_2H	358 (0.89) 260 (1.70)	440 (0.06) 363(0.68) 316 (1.26) 255 (3.39)	/
ML_2	360 (1.18) 266 (1.84)	489 (0.058) 362 (0.94) 320 (1.12) 255 (3.40)	414 (0.386) 493 (0.222)
$ML(OH)_2$	/	/	486(0.13)

Table S4. Spectrophotometric data (λ_{max} ($\varepsilon \times 10^4$) [nm (M^{-1} cm^{-1})] of pyochelin (**L**) Zn(II), Cu(II) and Fe(III) complexes. Solvent: CH_3OH/H_2O (80/20 by weight); I = 0.1 M; *T* = 25.0(2) °C. The uncertainties on the λ_{max} and $\varepsilon^{\lambda max}$ are 1 nm and 5%, respectively.