Tetraphosphonated thiophene ligand : mixing the soft and the hard for complexation

Jérémy Brandel,*[a] Alexandre Lecointre,[b] Julien Kollek,[b] Sylvia Michel,[a] Véronique Hubscher-Bruder,[a] Isabelle Déchamps,[c] Carlos Platas-Iglesias,[d] and Loïc J. Charbonnière*[b]

Supplementary Information (9 pages)

Table S1. log β^H values determined by UV-Vis absorption spectroscopy.

Table S2. Comparison of the values of the stability constants obtained with ligand L_T and Cu(II), Ni(II) and Zn(II) by potentiometry and by spectroscopy.

Table S3. Atomic coordinates of the optimized structures of $[Cu_2L_{T2}]^{12-}$

Figure S1. Potentiometric titration ($[L_T]_{tot} = 1.0 \times 10^{-3}$ M) vs pH (2.24 < p[H] < 12.82, Solvent: H_2O, I = 0.1 M ($NaClO_4$), T = 25.0(2) °C).

Figure S2. Electronic spectra of the protonated species of L_T. Solvent : H_2O; I = 0.1 M ($NaClO_4$); T = 25.0(2) °C.

Figure S3. Potentiometric titration of M:L_T (M = Cu(II), Zn(II), Ni(II), $[M]/[L_T] = 1$, $[L_T]_{tot} = 1.0 \times 10^{-3}$ M) vs pH (2.24 < p[H] < 11.82, Solvent: H_2O, I = 0.1 M ($NaClO_4$), T = 25.0(2) °C).

Fig. S4. Absorption titration curves vs pH of the Cu(II) complexes of L_T. $[L_T]_{tot} = 1.0 \times 10^{-4}$ M, l = 1cm for 220-420 nm and $[L_T] = 5.97\times10^{-4}$ M, l = 4 cm for 475-850 nm; $[M]/[L_T]=1$; 2.01 < p[H] < 12.59; Solvent: H_2O; I = 0.1 M ($NaClO_4$); T = 25.0(2) °C.

Fig. S5. Absorption titration curves vs pH of the Zn(II) complexes of L_T. $[L_T]_{tot} = 1.0 \times 10^{-4}$ M, l = 1 cm; $[Zn(II)]/[L_T]=1$; 2.21 < p[H] < 12.50; Solvent: H_2O; I = 0.1 M ($NaClO_4$); T = 25.0(2) °C.

Fig. S6. Absorption titration curves vs pH of the Ni(II) complexes of L_T. $[L_T]_{tot} = 1.0 \times 10^{-4}$ M, l = 1 cm; $[Ni(II)]/[L_T]=1$; 2.22 < pH < 12.45; Solvent: H_2O; I = 0.1 M ($NaClO_4$); T = 25.0(2) °C.

Fig. S7 Absorption titration curves of L_T by Cu(II) at pH 4.3. $[L_T]_{tot} = 1.0 \times 10^{-4}$ M; 0 < [Cu(II)]/[L] < 8.82; Solvent: acetate buffer 0.1M; l = 1cm; T = 25.0(2) °C.

Fig. S8 Calculated electronic spectra of the Cu:$\mathbf{L_T}$ species at pH 4.3. Solvent: acetate buffer 0.1M; l = 1cm; T = 25.0(2) °C.

Fig. S9 Distribution diagram of the Cu: $\mathbf{L_T}$ species and experimental data at 295 nm at pH 4.3 (acetate buffer, 0.1M). $[\mathbf{L_T}]_{tot} = 1.0 \times 10^{-4}$ M; 0 < [Cu(II)]/[$\mathbf{L_T}$] < 8.82; Solvent: acetate buffer 0.1M; l = 1cm; T = 25.0(2) °C.

Fig. S10. EPR spectra of a 1:1 mixture of Cu(II) and L_T as a function of the pH at 150 K in an EtOH/H_2O glassy matrix.

Table S1. log β^Hvalues determined by UV-Vis absorption spectroscopy.

LH	12.39(6)
LH_2	23.14
LH_3	30.1*
LH_4	36.2*
LH_5	/
LH_6	45.7(2)

$[L_T]_{tot} = 1.0 \times 10^{-4}$ M, l = 1 cm, Solvent: H_2O; I = 0.1 M ($NaClO_4$); T = 25.0(2) ◦C, 2.01 < p[H] < 12.59. Values are given with their standard deviation (s). Charges have been omitted for the sake of clarity. Values with * were fixed during refinement of the model.

Table S2. Comparison of the values of the stability constants obtained with ligand L_T and Cu(II), Ni(II) and Zn(II) by potentiometry and by spectroscopy.

	Log β	
	Spectro	**potentio**
NiL_T	10.3(4)	10.9(1)
NiL_TH	22.37(4)	21.56(2)
NiL_TH_2	30.77(9)	28.34(2)
NiL_TH_3	/	34.37(2)
NiL_TH_4	42.3(1)	39.42(4)
Ni(OH)	-8.1	
$Ni(OH)_2$	-16.47	

	Log β	
	Spectro	**potentio**
ZnL_T	10.98(4)	10.81(8)
ZnL_TH	22.68(4)	21.48(7)
ZnL_TH_2	30.0(2)	28.66(5)
ZnL_TH_3	35.22(6)	35.22(6)

ZnL_TH_4	40.6(3)	40.21(5)
Zn(OH)	-7.89	
$Zn(OH)_2$	-14.92	

	Log β	
	Spectro	**potentio**
CuL_T	16.6(2)	16.11(3)
CuL_TH	26.0(2)	26.09(3)
CuL_TH_2	32.7*	32.65(2)
CuL_TH_3	/	37.80(2)
CuL_TH_4	42.42(2)	42.25(2)
$CuL_T(OH)$	4.2(2)	/
Cu(OH)	-6.29	
$Cu(OH)_2$	-13.1	

Solvent: H_2O; I = 0.1 M ($NaClO_4$); T = 25.0(2) ◦C. Values are given with their standard deviation (s). Charges have been omitted for the sake of clarity. Values with * were fixed during refinement of the model.

Table S3. Atomic coordinates of the optimized structures of $[Cu_2L_{T2}]^{12-}$

$[Cu_2(L_T)_2]^{12-}$, TPSSh/SVP = imaginary frequencies

C	2.34481200	2.76504000	0.43352800
H	2.52722700	3.84865000	0.57704500
N	3.52783700	2.16515500	-0.23367800
C	3.70509400	2.53603100	-1.66718600
H	2.72378800	2.77185900	-2.10280400
H	4.35416100	3.43093700	-1.71813400
C	4.75799400	2.53890900	0.53326200
H	5.58835000	2.00649300	0.04033700
H	4.63551400	2.12128700	1.54376300
P	4.39784500	1.09230200	-2.61303700
P	5.27013100	4.36748400	0.69843200
O	4.05632200	5.11681200	1.32312500
O	6.48606200	4.23427400	1.65089200
O	5.63519600	4.85853700	-0.73250900
O	3.45872300	-0.08085100	-2.02151000
O	5.87011000	0.89456100	-2.20599200
O	4.11435100	1.32284700	-4.10229000
H	2.33330800	2.30984000	1.43844400
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C	4.97562400	-2.44153400	-0.28841600
H	5.13085000	-2.00455700	-1.28752100
N	3.56035700	-2.13823100	0.09573900

C	3.34696300	-2.49533800	1.52204800
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C	2.64248500	-2.82232200	-0.86863900
H	2.90397700	-2.39341200	-1.84674400
H	2.92082900	-3.89414100	-0.89381700
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O	3.06453200	0.11139600	1.81603600
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H	5.59957900	-1.88245700	0.42781200
C	1.03252700	2.48884900	-0.24495100
C	0.69479400	1.53042200	-1.17511800
S	-0.37392100	3.44770100	0.15777500
C	-0.67942900	1.57094900	-1.56039500
H	1.43934700	0.84361700	-1.59022500
C	-1.41374800	2.55006700	-0.93023600
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C	-2.85773900	2.89125600	-1.14584800
H	-3.10626400	2.66344100	-2.19425300
H	-3.05359200	3.96197000	-0.93722700
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O	7.05895400	-4.01487100	-0.83025500
O	5.55960900	-4.74298500	1.17144300
C	1.16827200	-2.60613400	-0.69043100
C	0.31892100	-1.92615700	-1.53555100
S	0.21725100	-3.34590600	0.58962500
C	-1.06076100	-1.96208000	-1.15609900
H	0.69142400	-1.40063200	-2.41656900
C	-1.28743100	-2.68702300	-0.00875800
H	-1.86782400	-1.45164000	-1.69172300
C	-2.54445300	-2.93979300	0.77119200
H	-2.84001100	-4.01090300	0.69373900
H	-2.37037800	-2.69550800	1.83332000
N	-3.71139400	-2.14263000	0.31403500
N	-3.82164400	2.11022300	-0.30198400
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H	-5.47470500	-1.30106400	1.06282100
H	-5.01376100	-2.78954600	1.88506400
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Cu	-3.27492600	-0.00136700	-0.09024800
P	-3.77007400	-0.76331400	2.73344000
P	-5.23452800	-4.53928700	-0.46952100
P	-4.86953300	4.53449800	1.00389600
P	-4.78884800	0.76756300	-2.54628100
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O                    -3.91468000    5.45508000    0.18175000
O                    -6.28548100    4.39158600    0.38284800
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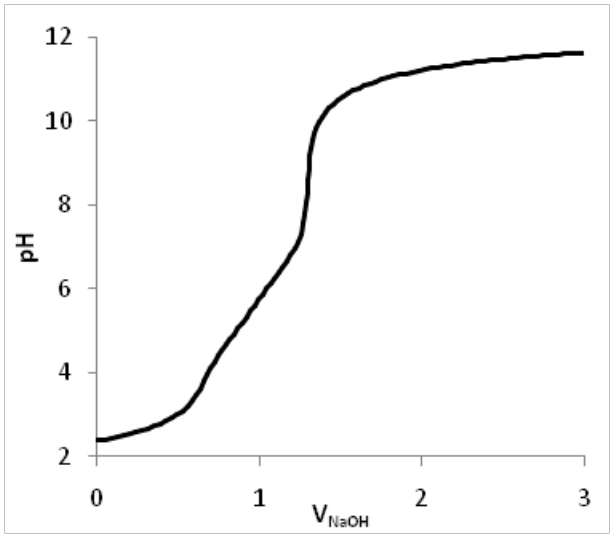

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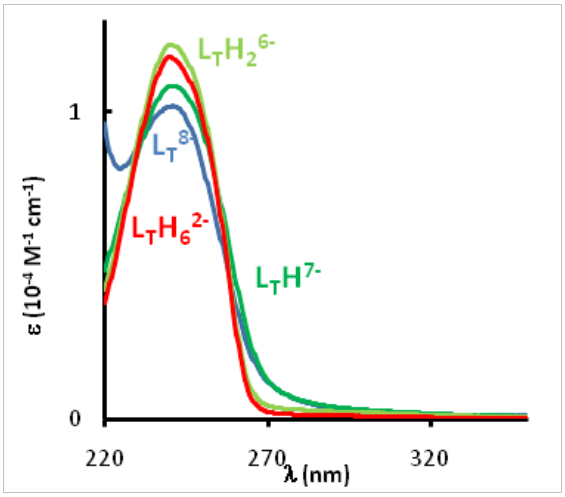


Figure S2. Electronic spectra of the protonated species of L_T. Solvent : H_2O; I = 0.1 M ($NaClO_4$); T = 25.0(2) °C.

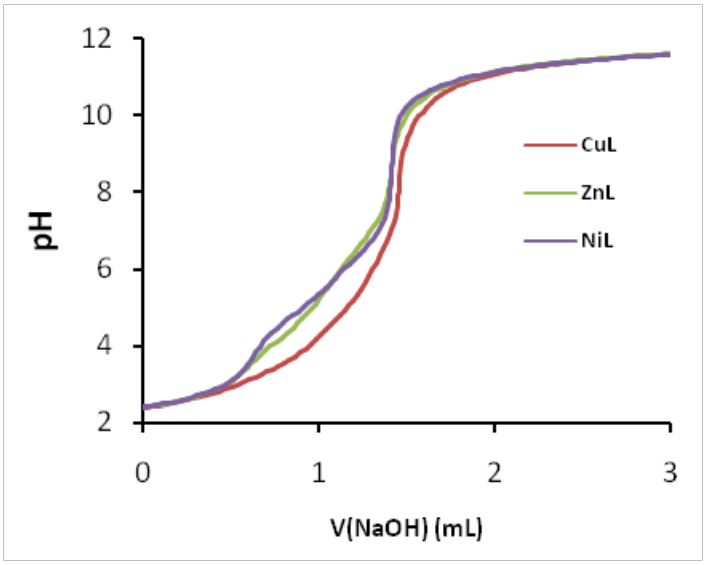
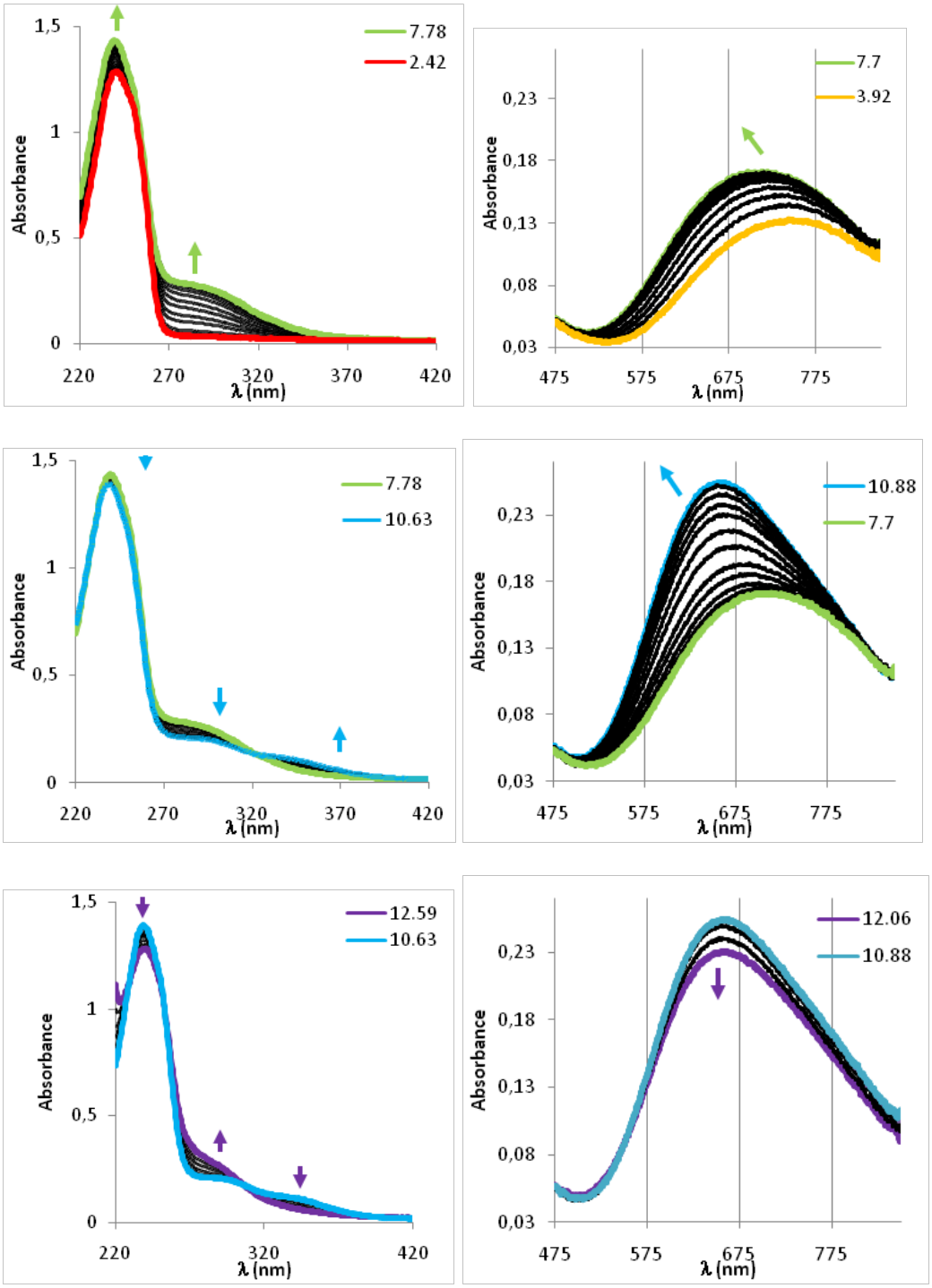


Figure S3. Potentiometric titration of M:L_T (M = Cu(II), Zn(II), Ni(II), [M]/[L_T] = 1, $[L_T]_{tot} = 1.0 \times 10^{-3}$ M) vs pH (2.24 < p[H] < 11.82, Solvent: H_2O, I = 0.1 M ($NaClO_4$), T = 25.0(2) °C).



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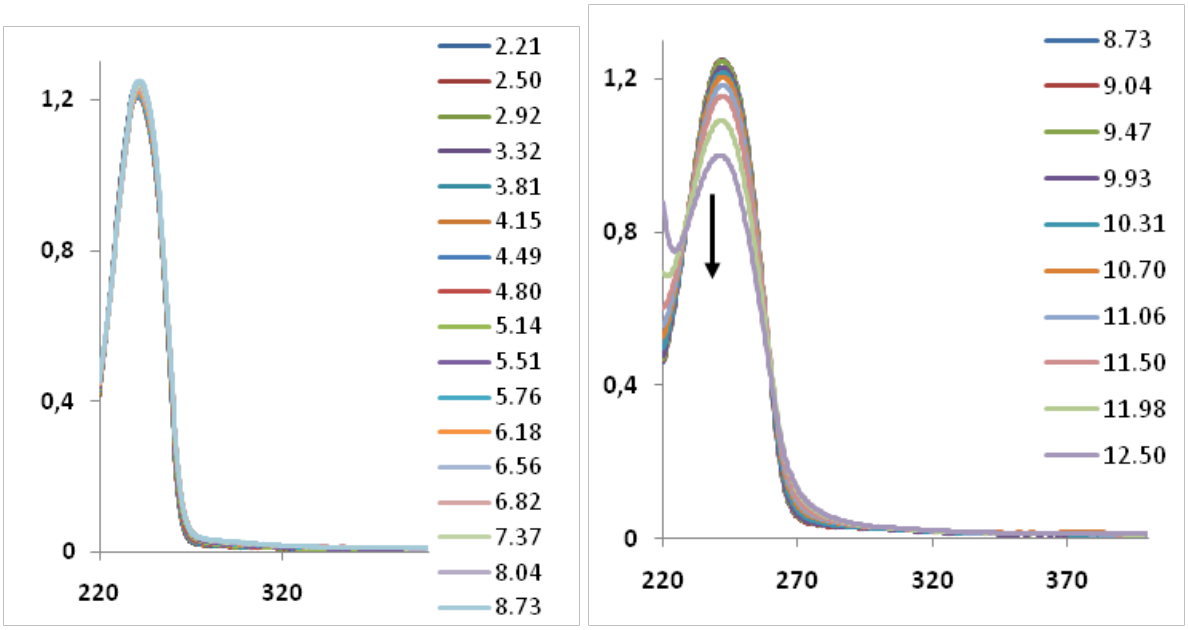

Fig. S5. Absorption titration curves vs pH of the Zn(II) complexes of L_T. $[L_T]_{tot} = 1.0 \times 10^{-4}$ M, l = 1 cm; $[Zn(II)]/[L_T]=1$; 2.21 < p[H] < 12.50; Solvent: H_2O; I = 0.1 M ($NaClO_4$); T = 25.0(2) °C.

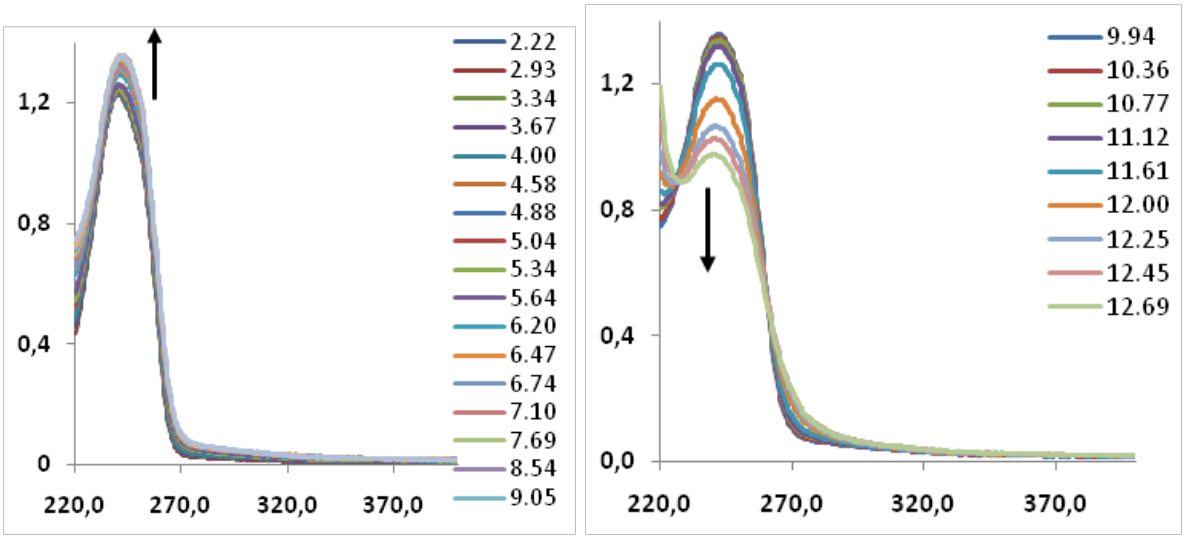

Fig. S6. Absorption titration curves vs pH of the Ni(II) complexes of L_T. $[L_T]_{tot} = 1.0 \times 10^{-4}$ M, l = 1 cm; $[Ni(II)]/[L_T]=1$; 2.22 < pH < 12.45; Solvent: H_2O; I = 0.1 M ($NaClO_4$); T = 25.0(2) °C.

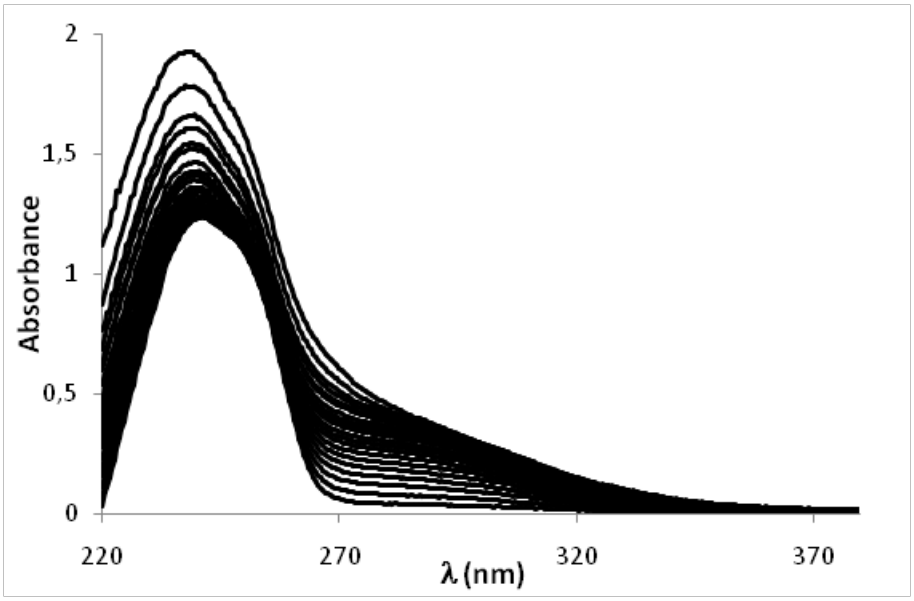

Fig. S7 Absorption titration curves of L_T by Cu(II) at pH 4.3. $[L_T]_{tot} = 1.0 \times 10^{-4}$ M; 0 < [Cu(II)]/[L] < 8.82; Solvent: acetate buffer 0.1M; l = 1cm; T = 25.0(2) °C.

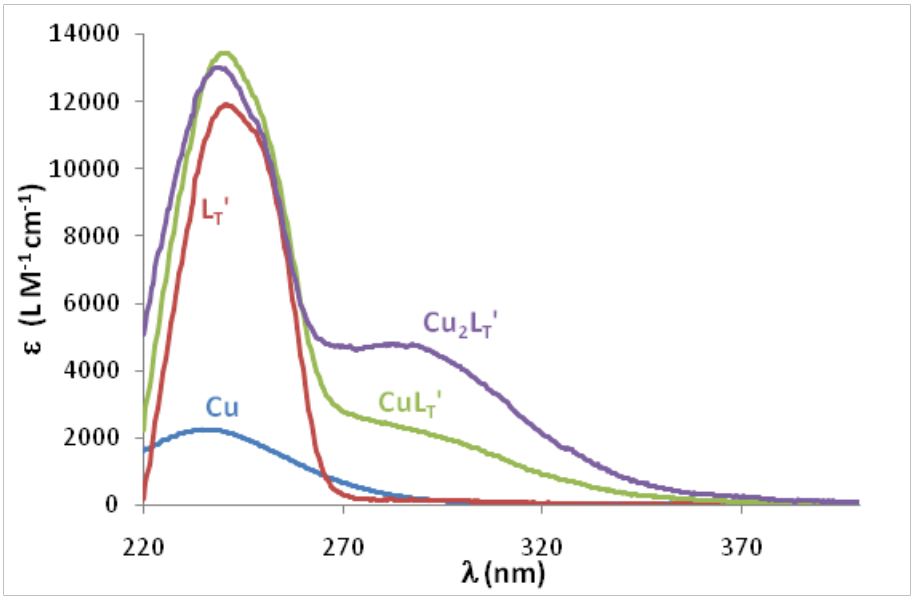

Fig. S8 Calculated electronic spectra of the Cu:$\mathbf{L_T}$ species at pH 4.3. Solvent: acetate buffer 0.1M; l = 1cm; T = 25.0(2) °C.

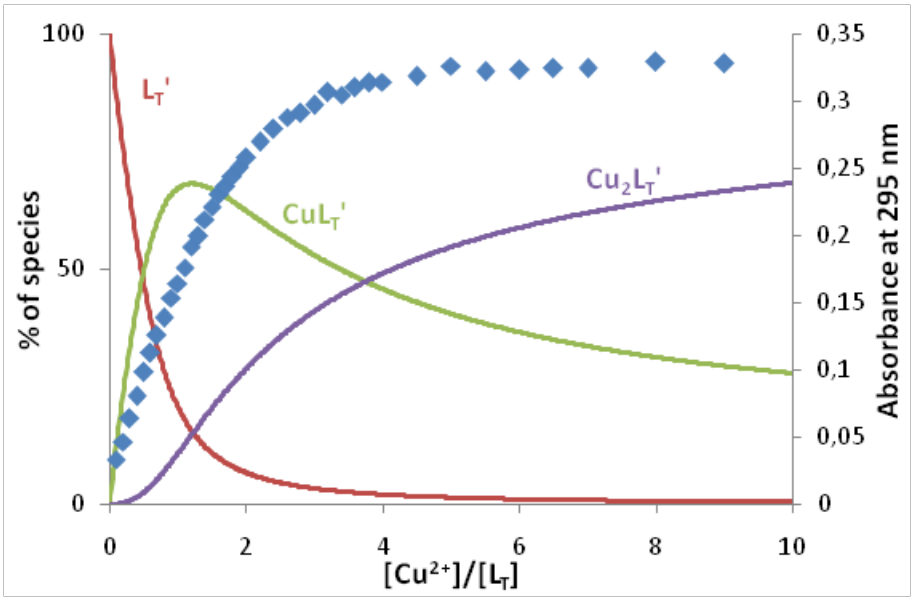

Fig. S9 Distribution diagram of the Cu: $\mathbf{L_T}$ species and experimental data at 295 nm at pH 4.3 (acetate buffer, 0.1M). $[\mathbf{L_T}]_{tot} = 1.0 \times 10^{-4}$ M; 0 < [Cu(II)]/[$\mathbf{L_T}$] < 8.82; Solvent: acetate buffer 0.1M; l = 1cm; T = 25.0(2) °C.

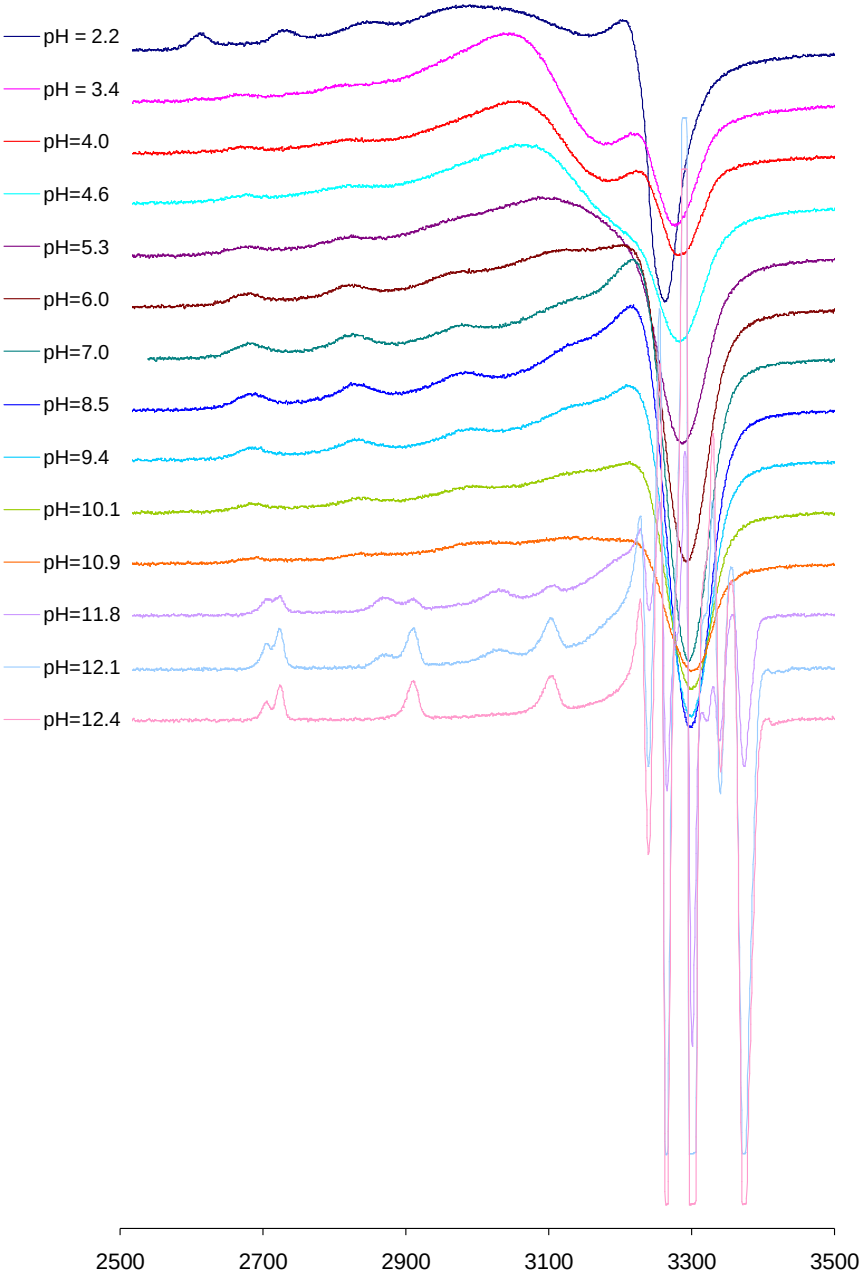

Fig. S10. EPR spectra of a 1:1 mixture of Cu(II) and L_T as a function of the pH at 150 K in an EtOH/H_2O glassy matrix.