Supporting Information

Synthesis, spectroscopy and binding constants of ketocatechol-containing iminodiacetic acid and its Fe(III), Cu(II) and Zn(II) complexes and reaction of Cu(II) complex with H_2O_2 in aqueous solution†

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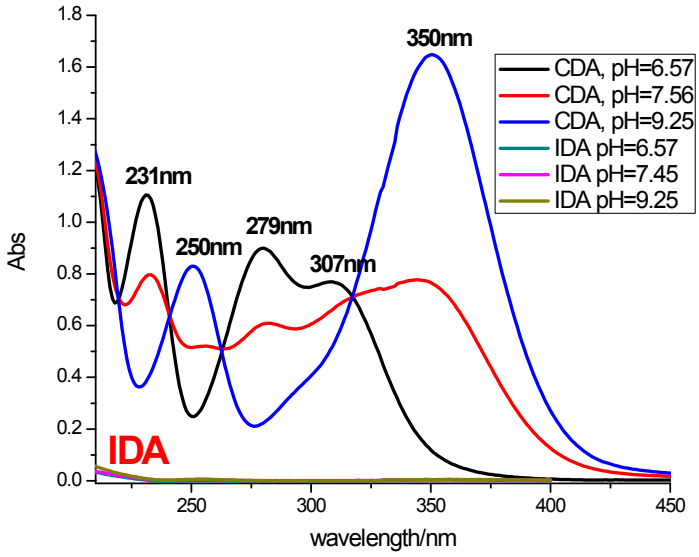

Fig. S1 UV spectrum of 1.00×10^{-4} M 2-chloro-3',4'-dihydroxyacetophenone (CDA) and IDA at different pH based NaOH (0.1M) at 25℃.

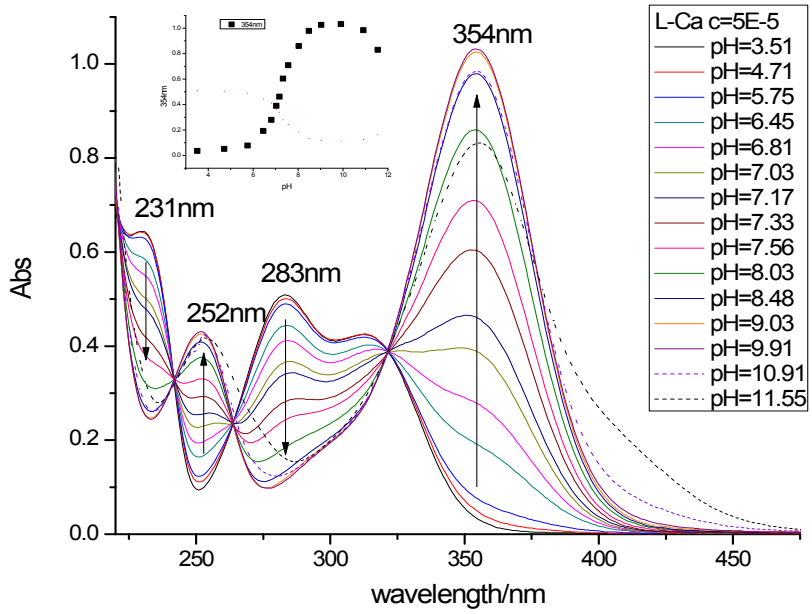

Fig. s2 UV spectrum of 5.00×10^{-5} M H_4L and 5.00×10^{-5} M $Ca(NO_3)_2$ at different pH. pH was adjusted with NaOH (0.1M) at 25℃. The inset figure is the absorbance at 354 nm at different pH.

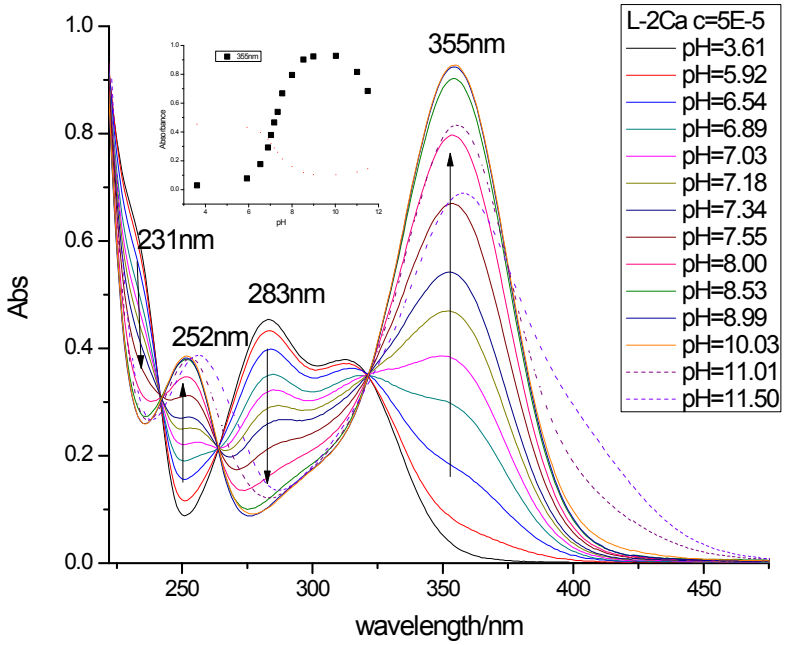

Fig. s3 UV spectrum of 5.00×10^{-5} M H_4L and 1.00×10^{-4} M $Ca(NO_3)_2$ at different pH. pH was adjusted with NaOH (0.1M) at 25℃. The inset figure is the absorbance at 355 nm at different pH.

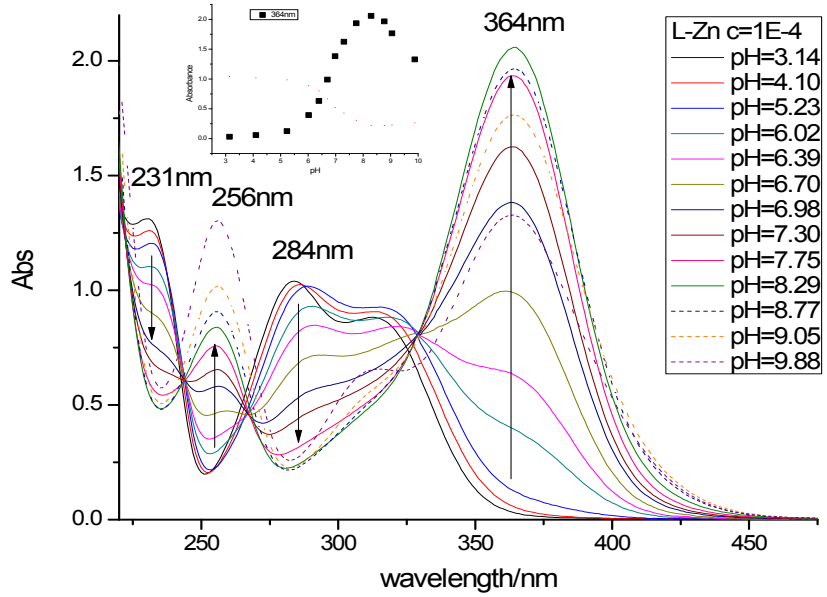

Fig. s4 UV spectrum of 1.00×10^{-4} M H_4L and 1.00×10^{-4} M $Zn(NO_3)_2$ at different pH. pH was adjusted with NaOH (0.1M) at 25℃. The inset figure is the absorbance at 364 nm at different pH.

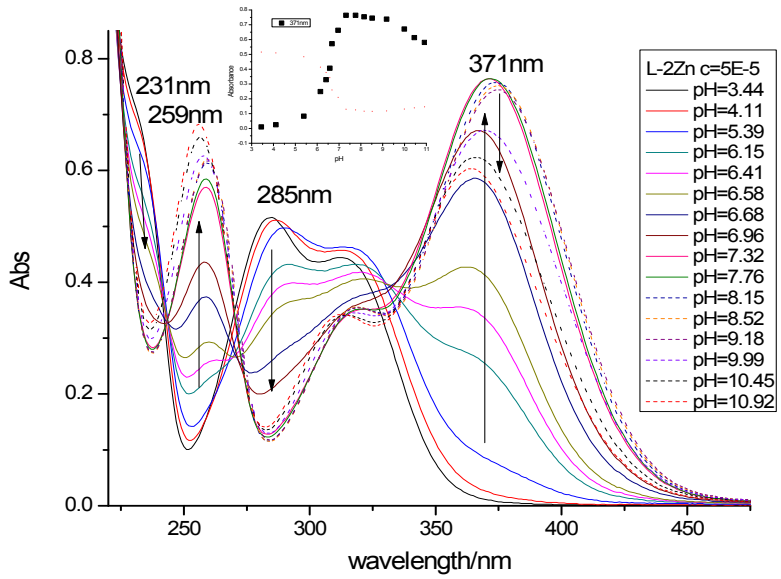

Fig. s5 UV spectrum of 5.00×10^{-5} M H_4L and 1.00×10^{-4} M $Zn(NO_3)_2$ at different pH. pH was adjusted with NaOH (0.1M) at 25℃. The inset figure is the absorbance at 371 nm at different pH.

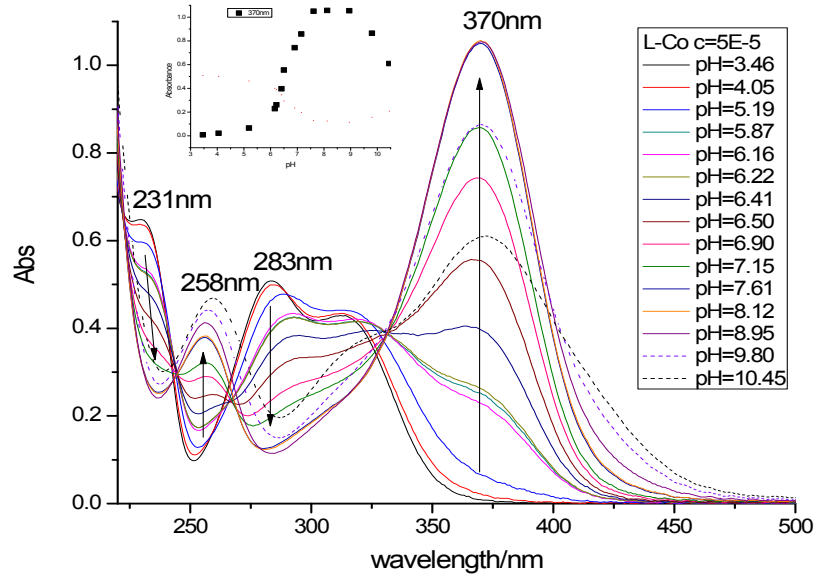

Fig. s6 UV spectrum of 5.00×10^{-5} M H_4L and 5.00×10^{-5} M $Co(NO_3)_2$ at different pH. pH was adjusted with NaOH (0.1M) at 25℃. The inset figure is the absorbance at 370 nm at different pH.

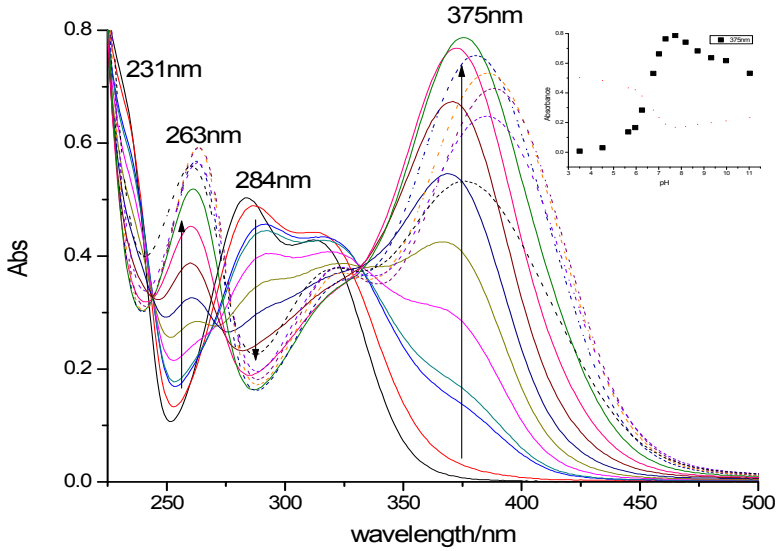

Fig. s7 UV spectrum of 5.00×10^{-5} M H_4L and 1.00×10^{-4} M $Co(NO_3)_2$ at different pH. pH was adjusted with NaOH (0.1M) at 25℃. The inset figure is the absorbance at 375 nm at different pH.

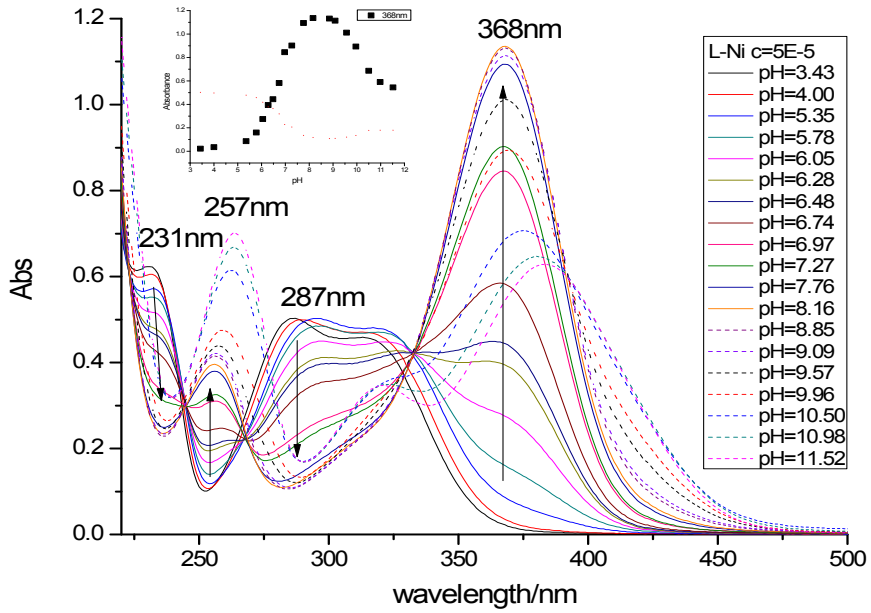

Fig. s8 UV spectrum of 5.00×10^{-5} M H_4L and 5.00×10^{-5} M $Ni(NO_3)_2$ at different pH. pH was adjusted with NaOH (0.1M) at 25℃. The inset figure is the absorbance at 368 nm at different pH.

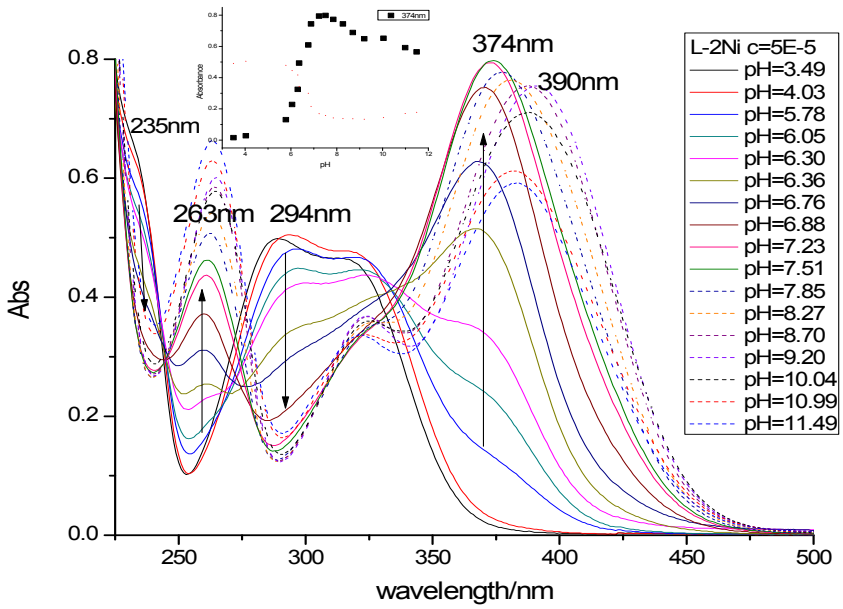

Fig. s9 UV spectrum of 5.00×10^{-5} M H_4L and 1.00×10^{-4} M $Ni(NO_3)_2$ at different pH. pH was adjusted with NaOH (0.1M) at 25℃. The inset figure is the absorbance at 374 nm at different pH.

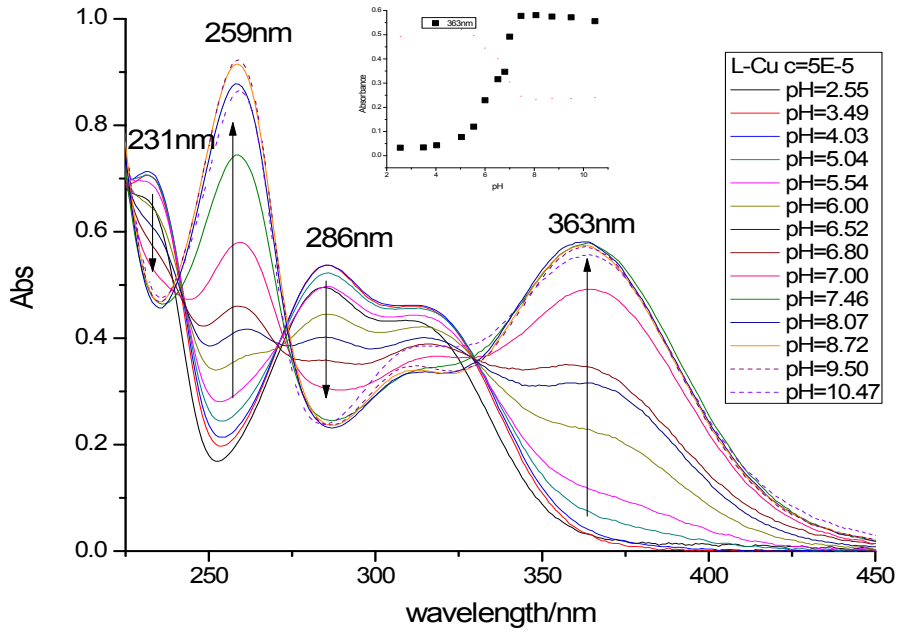

Fig. s10 UV spectrum of 5.00×10^{-5} M H_4L and 5.00×10^{-5} M $Cu(NO_3)_2$ at different pH. pH was adjusted with NaOH (0.1M) at 25℃. The inset figure is the absorbance at 363 nm at different pH.

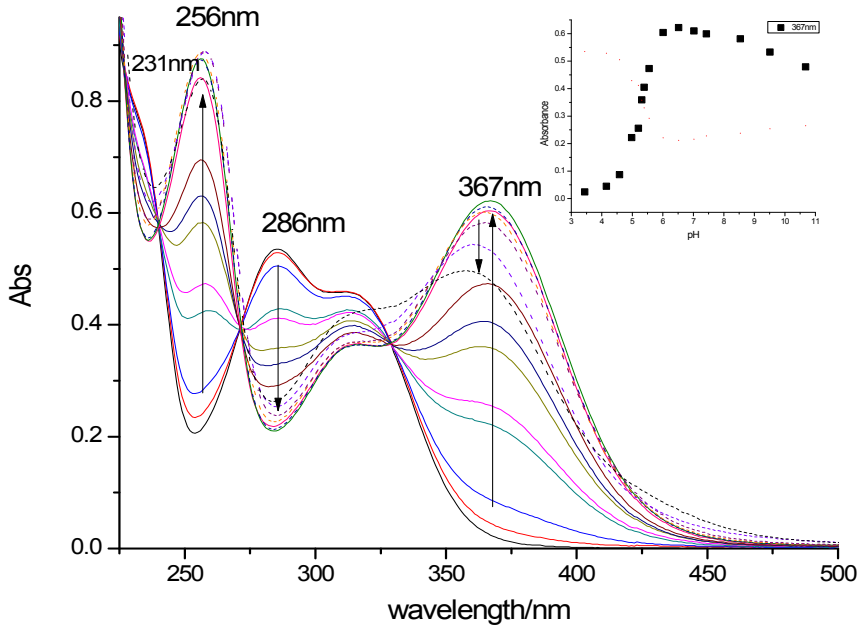

Fig. s11 UV spectrum of 5.00×10^{-5} M H_4L and 1.00×10^{-4} M $Cu(NO_3)_2$ at different pH. pH was adjusted with NaOH (0.1M) at 25℃. The inset figure is the absorbance at 367 nm at different pH.

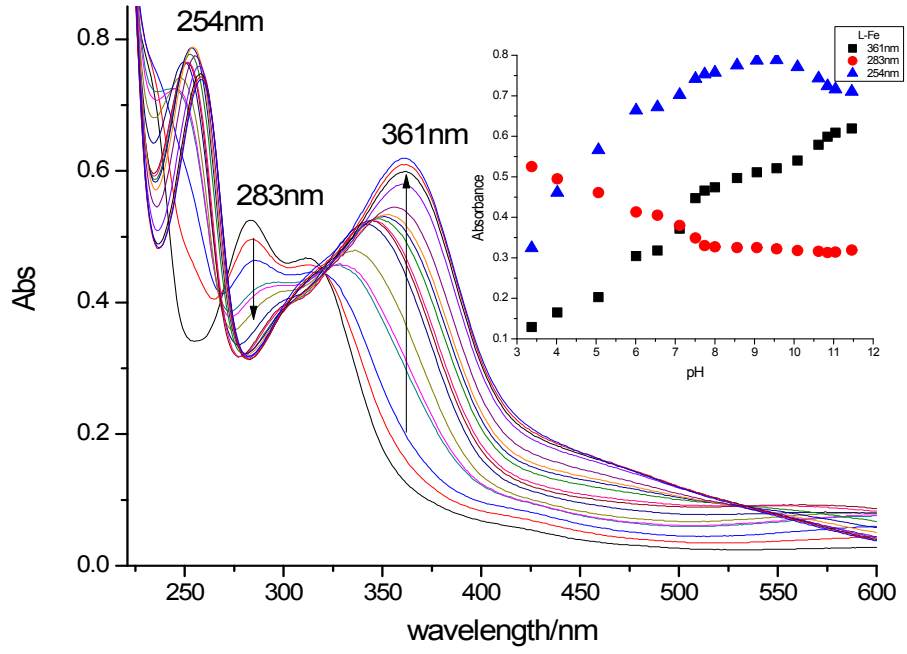

Fig. s12 UV spectrum of 5.00×10^{-5} M H_4L and 5.00×10^{-5} M $Fe(NO_3)_3$ at different pH. pH was adjusted with NaOH (0.1M) at 25℃. The inset figure is the absorbance at 361 (black), 283 (red) and 254 (blue) nm at different pH.

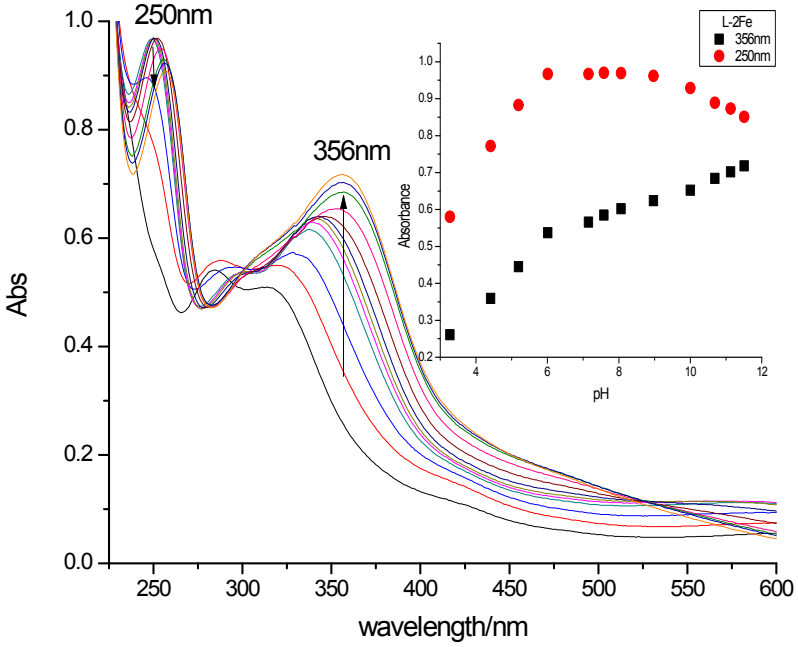

Fig. s13 UV spectrum of 5.00×10^{-5} M H_4L and 1.00×10^{-4} M $Fe(NO_3)_3$ at different pH. pH was adjusted with NaOH (0.1M) at 25℃. The inset figure is the absorbance at 356 (red) and 250 (black) nm at different pH.

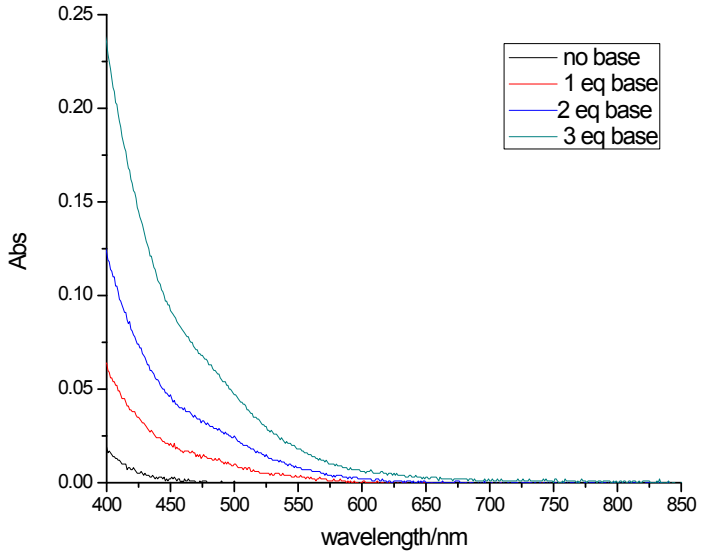

Fig. s14 UV-vis spectra of a 0.5 mM IDA and 0.5 mM $Fe(NO_3)_3$ aqueous solution with different amount NaOH.

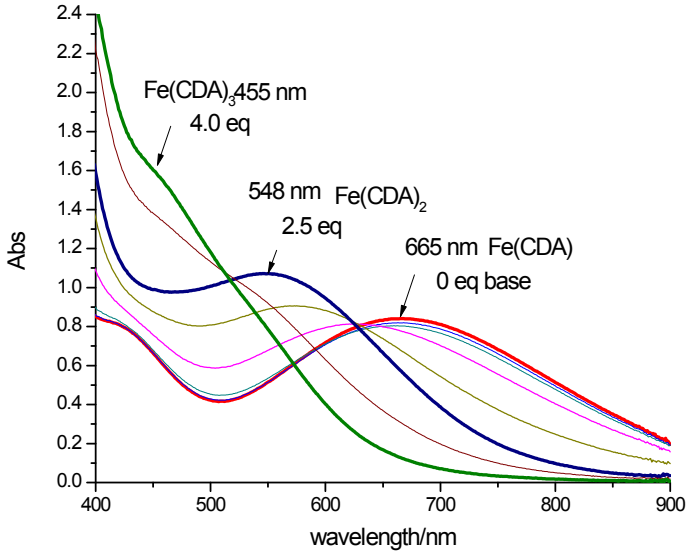

Fig. s15 UV-vis spectra of a 0.5 mM CDA and 0.5 mM $Fe(NO_3)_3$ aqueous solution with different amount NaOH. 0 equiv NaOH per Fe(III) formed {Fe(CDA)} species at 665 nm (ε_{665} = 1692) , 2.5 equiv NaOH per Fe(III) formed $\{Fe(CDA)_2\}$ species at 548 nm (ε_{548} = 4280) and 4.0 equiv NaOH per Fe(III) formed $\{Fe(CDA)_3\}$ species at 455 nm (ε_{455} = 9480).

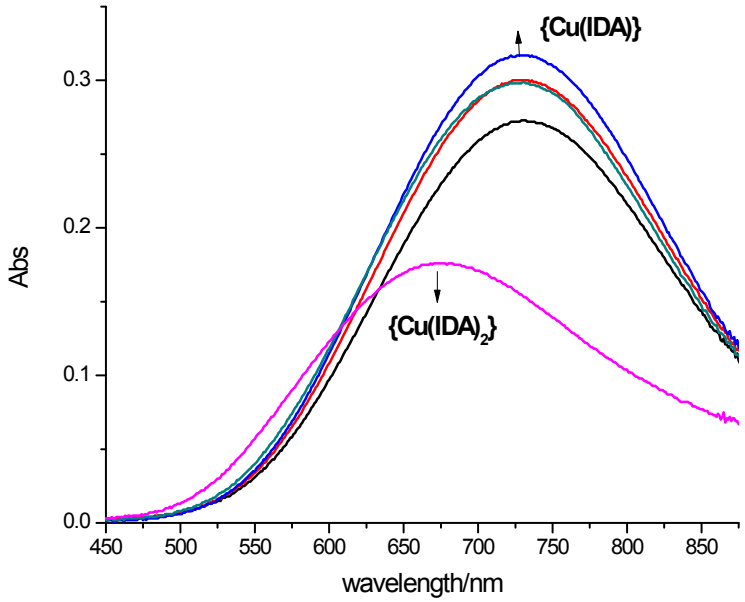

Fig. s16 UV-vis spectra of a 10 mM IDA and 5 mM $Cu(NO_3)_2$ aqueous solution with NaOH. 2.0 equiv NaOH per Cu(II) formed {Cu(IDA)} species at 726 nm (ε_{726} = 62) and 4.0 equiv NaOH per Cu(II) formed $\{Cu(IDA)_2\}$ species at 677 nm (ε_{677} = 36). Two species are all pale blue.

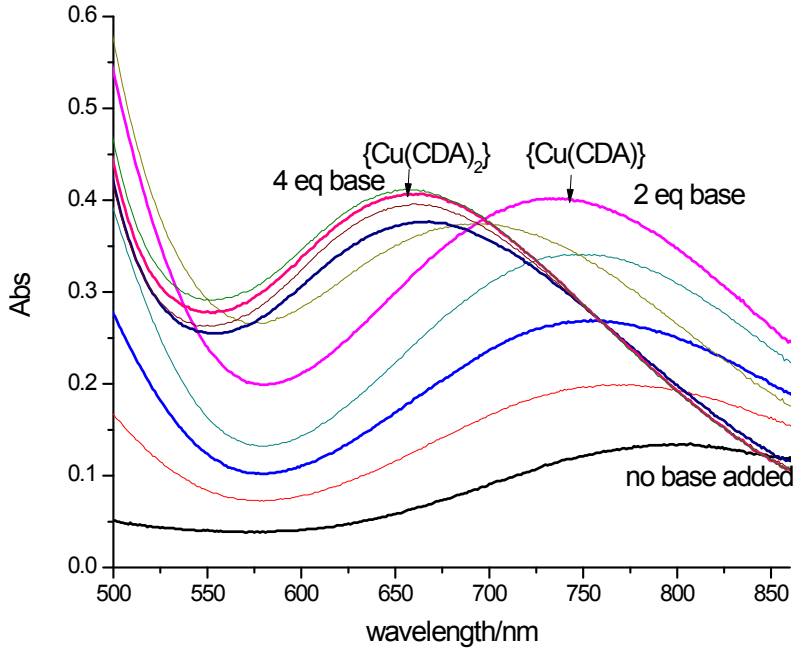

Fig. s17 UV-vis spectra of a 10 mM 2-chloro-3',4'-dihydroxyacetophenone(CDA) and 10 mM $Cu(NO_3)_2$ aqueous solution with NaOH. 2.0 equiv NaOH per Cu(II) formed {Cu(CDA)} species at 732 nm ($\varepsilon_{732} = 40$) and 4.0 equiv NaOH per Cu(II) formed {Cu $(CDA)_2$} species at 658 nm ($\varepsilon_{658} = 41$). The color of two species are dark yellow and dark green respectively.

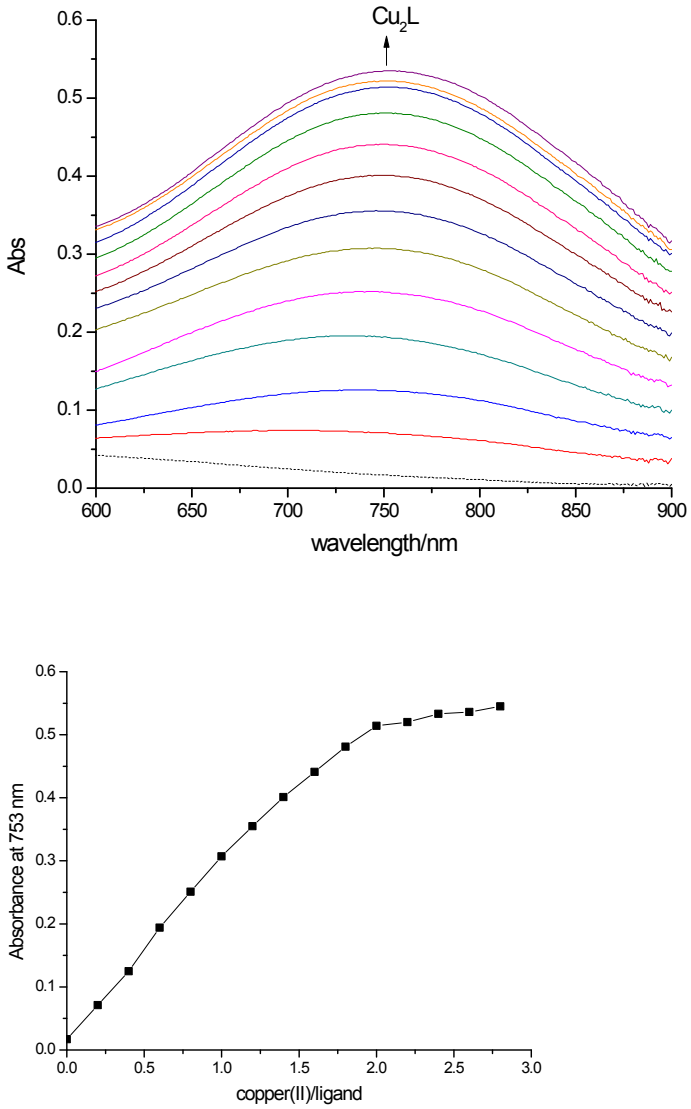

Fig. s18 UV-vis spectra of 5.00 mM H_4L with different amount $Cu(NO_3)_2$ in aqueous solution at pH 4.8 (top) . The absorbance/molar ratio plot with λ_{max} at 753 nm (bottom)

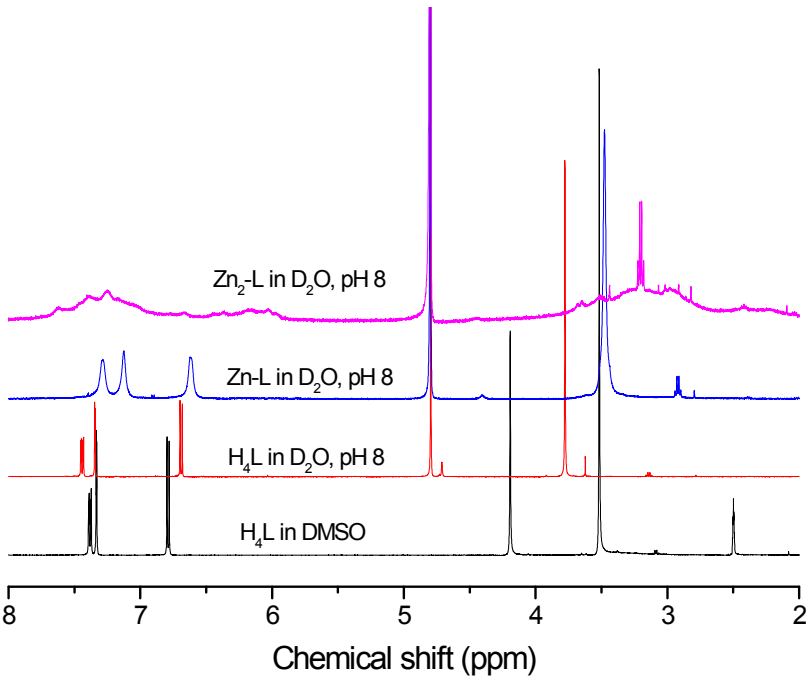

Fig. s19 ^{1}H NMR spectrum of H_4L in DMSO (1) and pH 8.0 D_2O solution. H_4L (2), Zn-L bright- yellow powder (3) and Zn_2-L green-yellow powder (4)

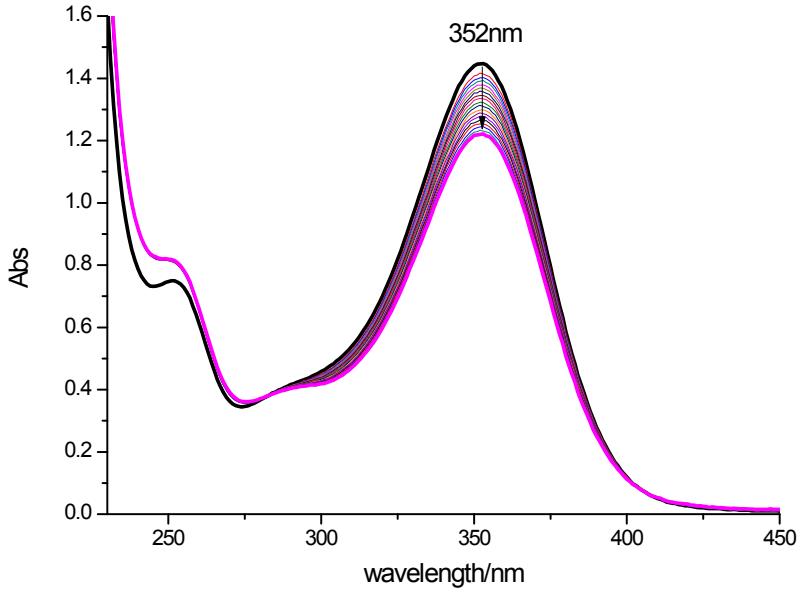

Fig. s 20 Spectra changes of $1.0x10^{-4}$ ligand in 50 mM HEPES buffer at pH=8.0, 50eq H_2O_2

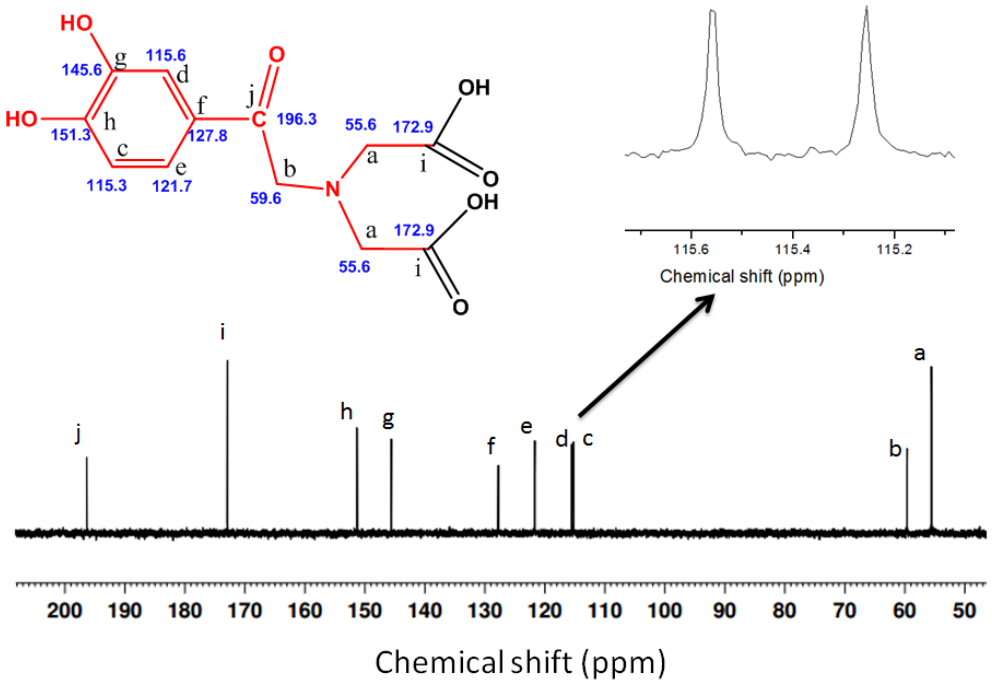

Fig. s 21 ^{13}C NMR of H_4L in DMSO

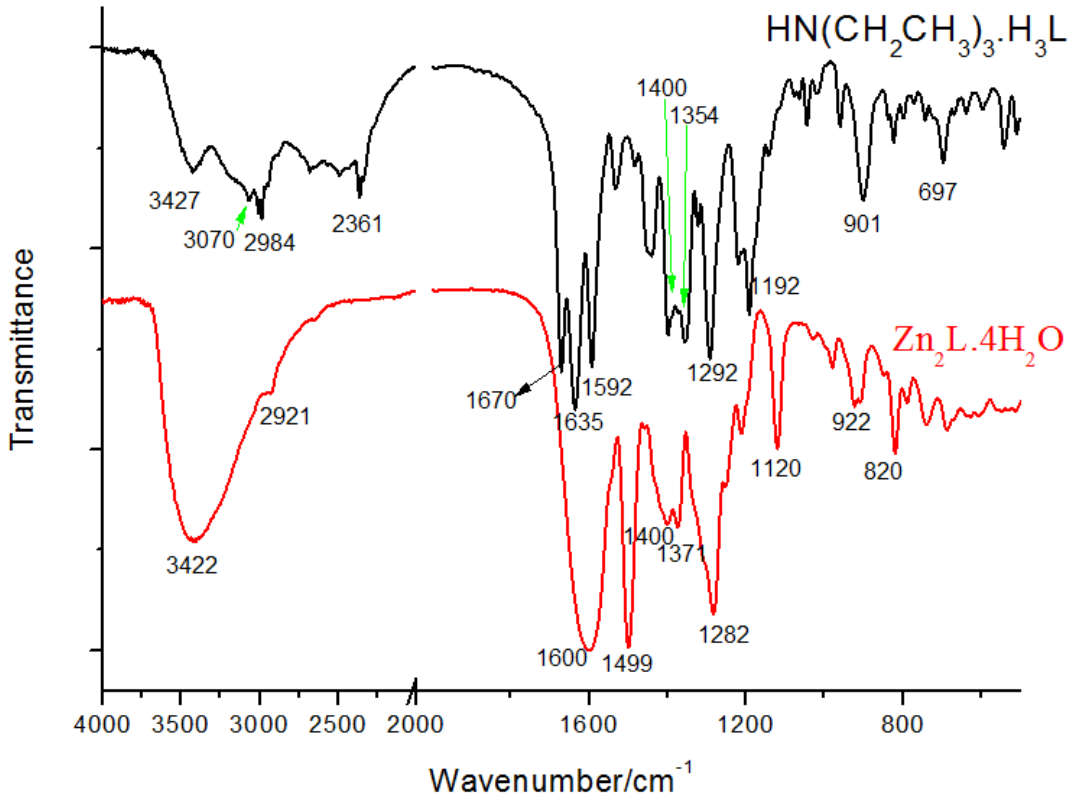

Fig. s 22 IR spectra of $HN(CH_2CH_3)_3 \cdot H_3L$ and $Zn_2L \cdot 4H_2O$ (KBr disc)

Table s1. Crystal data and structure refinement for $HN(CH_2CH_3)_3 \cdot H_3L$.

Identification code	$HN(CH_2CH_3)_3 \cdot H_3L$
Empirical formula	C18 H27 N2 O7
Formula weight	383.42
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.3882(14) A alpha = 71.834(2) deg. b = 11.1278(18) A beta = 79.964(2) deg. c = 11.3535(18) A gamma = 73.789(2) deg.
Volume	962.5(3) A^3
Z, Calculated density	2, 1.323 Mg/m^3
Absorption coefficient	0.102 mm^{-1}
F(000)	410
Crystal size	0.13 x 0.04 x 0.02 mm
Theta range for data collection	1.90 to 25.00 deg.
Limiting indices	-9<=h<=9, -13<=k<=4, -13<=l<=10
Reflections collected / unique	4320 / 3243 [R(int) = 0.0228]
Completeness to theta = 25.00	95.7 %
Max. and min. transmission	0.9980 and 0.9869
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3243 / 0 / 262
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0819, wR2 = 0.1897
R indices (all data)	R1 = 0.1246, wR2 = 0.2355
Extinction coefficient	0.011(5)
Largest diff. peak and hole	0.420 and -0.230 $e.A^{-3}$

Table. S2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 × 10^3) for $HN(CH_2CH_3)_3 \cdot H_3L$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	1970(6)	−1503(4)	4576(4)	58(1)
C(2)	2146(6)	−2409(4)	5755(4)	57(1)
C(3)	2590(5)	−2074(4)	6702(4)	54(1)
C(4)	2825(5)	−833(4)	6504(4)	52(1)
C(5)	2634(7)	62(4)	5341(4)	69(1)
C(6)	2221(7)	−285(4)	4385(4)	71(1)
C(7)	3235(6)	−505(4)	7551(4)	56(1)
C(8)	3086(6)	918(4)	7442(4)	54(1)
C(9)	3698(5)	2315(4)	8568(4)	49(1)
C(10)	2471(6)	3588(4)	8004(4)	52(1)
C(11)	1681(5)	908(4)	9561(4)	50(1)
C(12)	2084(6)	252(4)	10892(4)	49(1)
C(13)	2003(8)	4663(6)	3959(6)	98(2)
C(14)	3572(8)	3959(7)	4481(6)	109(2)
C(15)	2043(9)	3398(6)	2502(6)	110(2)
C(16)	1170(9)	3370(7)	1494(6)	116(2)
C(17A)	3070(30)	5590(30)	1920(20)	121(7)
C(18A)	2800(20)	6082(17)	593(15)	128(5)
C(17B)	2900(50)	5200(40)	1560(30)	121(7)
C(18B)	2720(30)	6600(20)	1280(20)	128(5)
N(1)	3194(4)	1092(3)	8672(3)	44(1)
N(2)	1864(5)	4734(4)	2624(4)	67(1)
O(1)	1499(5)	−1868(3)	3688(3)	76(1)
O(2)	1855(5)	−3589(3)	5891(3)	76(1)
O(3)	3683(5)	−1322(3)	8516(3)	75(1)
O(4)	879(4)	−34(3)	11646(3)	68(1)
O(5)	3524(4)	73(3)	11135(3)	64(1)
O(6)	2961(4)	4585(3)	7912(3)	72(1)
O(7)	1152(4)	3559(3)	7676(3)	66(1)

Table. S3 Bond lengths [A] and angles [deg] for $HN(CH_2CH_3)_3 \cdot H_3L$.

C(1)-O(1)	1.349(5)
C(1)-C(6)	1.374(6)
C(1)-C(2)	1.406(6)
C(2)-O(2)	1.359(5)
C(2)-C(3)	1.378(5)
C(3)-C(4)	1.392(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.388(6)
C(4)-C(7)	1.465(6)
C(5)-C(6)	1.383(6)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-O(3)	1.225(5)
C(7)-C(8)	1.521(5)
C(8)-N(1)	1.489(5)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-N(1)	1.499(5)
C(9)-C(10)	1.525(5)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-O(7)	1.239(5)
C(10)-O(6)	1.256(5)
C(11)-N(1)	1.497(5)
C(11)-C(12)	1.512(5)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-O(5)	1.234(5)
C(12)-O(4)	1.251(5)
C(13)-C(14)	1.451(8)
C(13)-N(2)	1.517(7)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(16)	1.475(8)
C(15)-N(2)	1.499(7)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700

C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17A)-C(18A)	1.47(3)
C(17A)-N(2)	1.54(2)
C(17A)-H(17A)	0.9700
C(17A)-H(17B)	0.9700
C(18A)-H(18A)	0.9600
C(18A)-H(18B)	0.9600
C(18A)-H(18C)	0.9600
C(17B)-N(2)	1.41(4)
C(17B)-C(18B)	1.46(5)
C(17B)-H(17C)	0.9700
C(17B)-H(17D)	0.9700
C(18B)-H(18D)	0.9600
C(18B)-H(18E)	0.9600
C(18B)-H(18F)	0.9600
N(1)-H(1N)	0.89(4)
O(1)-H(1)	0.8200
O(2)-H(2)	0.8200

O(1)-C(1)-C(6)	123.0(4)
O(1)-C(1)-C(2)	117.5(4)
C(6)-C(1)-C(2)	119.5(4)
O(2)-C(2)-C(3)	123.6(4)
O(2)-C(2)-C(1)	116.7(4)
C(3)-C(2)-C(1)	119.7(4)
C(2)-C(3)-C(4)	120.4(4)
C(2)-C(3)-H(3)	119.8
C(4)-C(3)-H(3)	119.8
C(5)-C(4)-C(3)	119.6(4)
C(5)-C(4)-C(7)	122.0(4)
C(3)-C(4)-C(7)	118.4(4)
C(6)-C(5)-C(4)	119.9(4)
C(6)-C(5)-H(5)	120.0
C(4)-C(5)-H(5)	120.0
C(1)-C(6)-C(5)	120.8(4)
C(1)-C(6)-H(6)	119.6
C(5)-C(6)-H(6)	119.6
O(3)-C(7)-C(4)	123.2(4)
O(3)-C(7)-C(8)	118.2(4)
C(4)-C(7)-C(8)	118.6(4)
N(1)-C(8)-C(7)	110.8(3)
N(1)-C(8)-H(8A)	109.5

C(7)-C(8)-H(8A)	109.5
N(1)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	108.1
N(1)-C(9)-C(10)	115.8(3)
N(1)-C(9)-H(9A)	108.3
C(10)-C(9)-H(9A)	108.3
N(1)-C(9)-H(9B)	108.3
C(10)-C(9)-H(9B)	108.3
H(9A)-C(9)-H(9B)	107.4
O(7)-C(10)-O(6)	126.8(4)
O(7)-C(10)-C(9)	119.7(4)
O(6)-C(10)-C(9)	113.5(4)
N(1)-C(11)-C(12)	113.0(3)
N(1)-C(11)-H(11A)	109.0
C(12)-C(11)-H(11A)	109.0
N(1)-C(11)-H(11B)	109.0
C(12)-C(11)-H(11B)	109.0
H(11A)-C(11)-H(11B)	107.8
O(5)-C(12)-O(4)	126.7(4)
O(5)-C(12)-C(11)	118.3(4)
O(4)-C(12)-C(11)	115.0(4)
C(14)-C(13)-N(2)	118.0(5)
C(14)-C(13)-H(13A)	107.8
N(2)-C(13)-H(13A)	107.8
C(14)-C(13)-H(13B)	107.8
N(2)-C(13)-H(13B)	107.8
H(13A)-C(13)-H(13B)	107.1
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-N(2)	114.5(5)
C(16)-C(15)-H(15A)	108.6
N(2)-C(15)-H(15A)	108.6
C(16)-C(15)-H(15B)	108.6
N(2)-C(15)-H(15B)	108.6
H(15A)-C(15)-H(15B)	107.6
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5

H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18A)-C(17A)-N(2)	109.7(14)
C(18A)-C(17A)-H(17A)	109.7
N(2)-C(17A)-H(17A)	109.7
C(18A)-C(17A)-H(17B)	109.7
N(2)-C(17A)-H(17B)	109.7
H(17A)-C(17A)-H(17B)	108.2
N(2)-C(17B)-C(18B)	112(3)
N(2)-C(17B)-H(17C)	109.2
C(18B)-C(17B)-H(17C)	109.2
N(2)-C(17B)-H(17D)	109.2
C(18B)-C(17B)-H(17D)	109.2
H(17C)-C(17B)-H(17D)	107.9
C(17B)-C(18B)-H(18D)	109.5
C(17B)-C(18B)-H(18E)	109.5
H(18D)-C(18B)-H(18E)	109.5
C(17B)-C(18B)-H(18F)	109.5
H(18D)-C(18B)-H(18F)	109.5
H(18E)-C(18B)-H(18F)	109.5
C(8)-N(1)-C(11)	112.7(3)
C(8)-N(1)-C(9)	113.2(3)
C(11)-N(1)-C(9)	113.8(3)
C(8)-N(1)-H(1N)	108(3)
C(11)-N(1)-H(1N)	107(3)
C(9)-N(1)-H(1N)	102(3)
C(17B)-N(2)-C(15)	98.9(16)
C(17B)-N(2)-C(13)	127.2(11)
C(15)-N(2)-C(13)	110.3(4)
C(17B)-N(2)-C(17A)	28.9(14)
C(15)-N(2)-C(17A)	123.1(11)
C(13)-N(2)-C(17A)	100.6(9)
C(1)-O(1)-H(1)	109.5
C(2)-O(2)-H(2)	109.5

Table. S4 Anisotropic displacement parameters ($A^2 \times 10^3$) for $HN(CH_2CH_3)_3 \cdot H_3L$. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [\ h^2\ a^{*2}\ U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U11	U22	U33	U23	U13	U12
C(1)	85(3)	47(2)	45(2)	-13(2)	-11(2)	-19(2)
C(2)	79(3)	41(2)	57(3)	-14(2)	-9(2)	-23(2)
C(3)	75(3)	38(2)	50(2)	-7(2)	-14(2)	-15(2)
C(4)	68(3)	41(2)	50(2)	-12(2)	-11(2)	-14(2)
C(5)	117(4)	47(3)	52(3)	-4(2)	-19(3)	-35(3)
C(6)	125(4)	47(3)	46(3)	-4(2)	-19(3)	-30(3)
C(7)	75(3)	41(2)	55(3)	-13(2)	-14(2)	-16(2)
C(8)	79(3)	41(2)	47(2)	-10(2)	-16(2)	-18(2)
C(9)	58(2)	38(2)	56(2)	-12(2)	-17(2)	-15(2)
C(10)	70(3)	39(2)	47(2)	-10(2)	-9(2)	-14(2)
C(11)	54(2)	48(2)	49(2)	-6(2)	-10(2)	-21(2)
C(12)	64(3)	40(2)	46(2)	-13(2)	-9(2)	-16(2)
C(13)	92(4)	103(5)	112(5)	-59(4)	-25(4)	0(4)
C(14)	114(5)	108(5)	101(5)	-32(4)	-32(4)	-4(4)
C(15)	142(6)	77(4)	113(5)	-51(4)	-45(4)	18(4)
C(16)	145(6)	99(5)	120(5)	-64(4)	-5(5)	-23(4)
C(17A)	102(8)	160(20)	99(16)	0(10)	-19(9)	-63(9)
C(18A)	154(9)	115(11)	109(12)	16(8)	-45(10)	-58(9)
C(17B)	102(8)	160(20)	99(16)	0(10)	-19(9)	-63(9)
C(18B)	154(9)	115(11)	109(12)	16(8)	-45(10)	-58(9)
N(1)	55(2)	36(2)	44(2)	-8(2)	-16(2)	-13(2)
N(2)	75(3)	54(2)	70(3)	-21(2)	-8(2)	-9(2)
O(1)	133(3)	56(2)	53(2)	-11(2)	-30(2)	-34(2)
O(2)	129(3)	44(2)	67(2)	-9(2)	-33(2)	-33(2)
O(3)	120(3)	41(2)	67(2)	-3(2)	-40(2)	-18(2)
O(4)	75(2)	82(2)	50(2)	-8(2)	-8(2)	-32(2)
O(5)	55(2)	81(2)	51(2)	-12(2)	-15(1)	-7(2)
O(6)	92(2)	44(2)	90(2)	-11(2)	-30(2)	-25(2)
O(7)	66(2)	45(2)	87(2)	-10(2)	-23(2)	-12(2)

Table. S5 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($A^2 \times 10^3$) for $HN(CH_2CH_3)_3 \cdot H_3L$.

	x	y	z	U(eq)
H(3)	2734	-2680	7477	65
H(5)	2784	894	5204	83
H(6)	2111	314	3604	85
H(8A)	3973	1219	6851	65
H(8B)	2029	1440	7133	65
H(9A)	4762	2300	8066	58
H(9B)	3867	2309	9394	58
H(11A)	1123	387	9307	60
H(11B)	916	1751	9516	60
H(13A)	1764	5549	4017	118
H(13B)	1134	4270	4482	118
H(14A)	3843	3079	4428	163
H(14B)	3473	3954	5338	163
H(14C)	4438	4377	4024	163
H(15A)	3219	3002	2358	132
H(15B)	1620	2871	3284	132
H(16A)	10	3787	1609	174
H(16B)	1284	2482	1510	174
H(16C)	1649	3822	706	174
H(17A)	2888	6322	2269	145
H(17B)	4213	5091	2023	145
H(18A)	3554	5505	154	191
H(18B)	3008	6937	261	191
H(18C)	1674	6122	496	191
H(17C)	2630	5003	855	145
H(17D)	4054	4749	1696	145
H(18D)	1737	7054	853	191
H(18E)	3680	6829	750	191
H(18F)	2627	6831	2034	191
H(1N)	4060(50)	480(40)	9010(40)	62(14)
H(1)	1417	-1266	3046	115
H(2)	2117	-4081	6570	114

Table S6 Hydrogen bonds for $HN(CH_2CH_3)_3 \cdot H_3L$ [Å and□.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(5)#1	0.95(4)	1.889(5)	2.703(5)	142.1(5)
O(2)-H(2)...O(6)#4	0.821(3)	1.853(3)	2.658(4)	166.7(3)
O(1)-H(1)...O(4)#3	0.820(3)	1.782(3)	2.588(4)	167.0(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+2; #2 -x,-y+1,-z+1; #3 x,y,z-1; #4 x,y-1,z