Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

A highly selective colorimetric chemosensor for cobalt(II) ion based on a tripodal amide ligand

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General Methods

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV 500 NMR spectrometer. ^{1}H NMR spectra were registered in $CDCl_3$, and chemical shifts are expressed in parts per million (δ) relative to internal Me_4Si. All coupling constants are absolute values and J values are expressed in Hertz (Hz). The description of signals include: s = singlet, bs = broad singlet, d = doublet, m = multiplet, dd = doublet of doublets. HR-MS spectra were recorded on a Bruker En Apex ultra 7.0T FT-MS apparatus. IR spectra were recorded on a Nicolet Avatar 360FT-IR spectrometer as KBr disks.

All reagents were of commercial origin and were used as received. Tetrahydrofuran (THF) was distilled prior to use from benzophenone. Silica gel (zhifu, 300-400 mesh) from Yantai silica gel factory (China) was used for column chromatography, eluting (unless otherwise stated) with ethyl acetate.

The acylating chlorination of the 5-(Methoxycarbonyl) Picolinic Acid was prepared as follows: The entire reaction vessel was dried to remove the water beforehand. At 75 °C, 10 mL (A.R.) $SOCl_2$ was slowly added to the 5-(Methoxycarbonyl) picolinic Acid (0.543 g, 3 mmol). The solution was refluxed for 7 h at 75 °C。Excess thionyl chloride was then removed in vacuum under stirring to get the acid chloride.

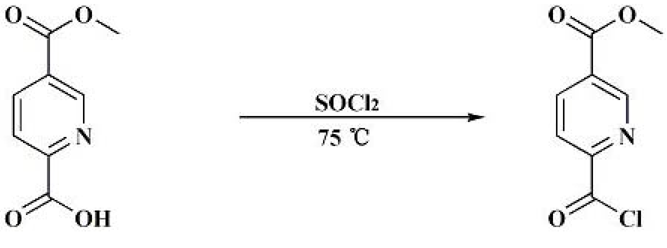


Figure S1. The acylating chlorination of the 5-(Methoxycarbonyl) picolinic Acid

The detailed synthesis method of Tris{2-carbamoyl-(5-carbomethoxy-pyridine-2) ethyl}amine (**H_3L, 1**): Et_3N (0.5 mL , to remove excess acid) was added to a dry flask filled with acid chloride (0.597 g, 3 mmol) was added in anhydrous THF (30 mL) slowly under N_2 protection, then Tris(2-aminoethyl)amine (0.15 ml, 1 mmol) was added dropwise. The solution turned yellow. The solution stirred for 24 h under room temperature. Then saturated aqueous NH_4Cl (10 mL) was added and the solution was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. After concentration in vacuum, the residue was purified by flash chromatography on silica gel with $CH_3COOC_2H_5$ to afford **H_3L** as a colorless solid in a 40 % yield.

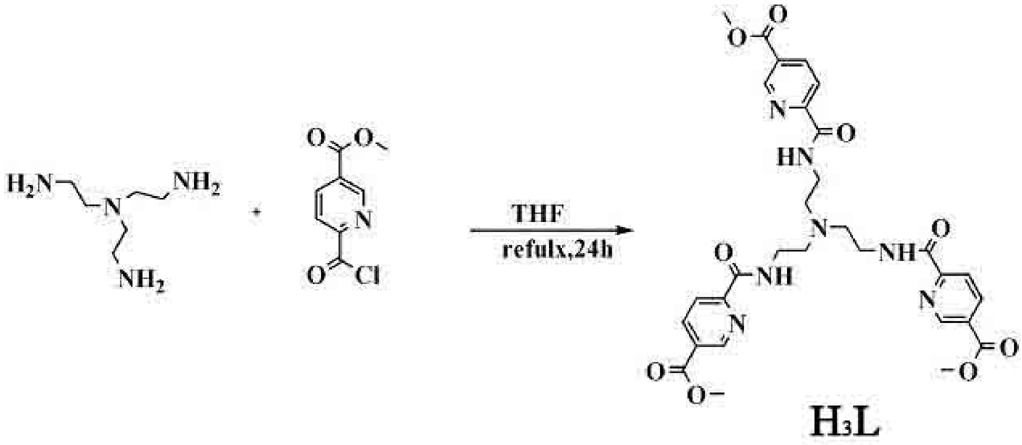


Figure S2. Synthesis of Tris{2-carbamoyl-(5-carbomethoxy-pyridine-2)ethyl}amine (**H_3L, 1**)

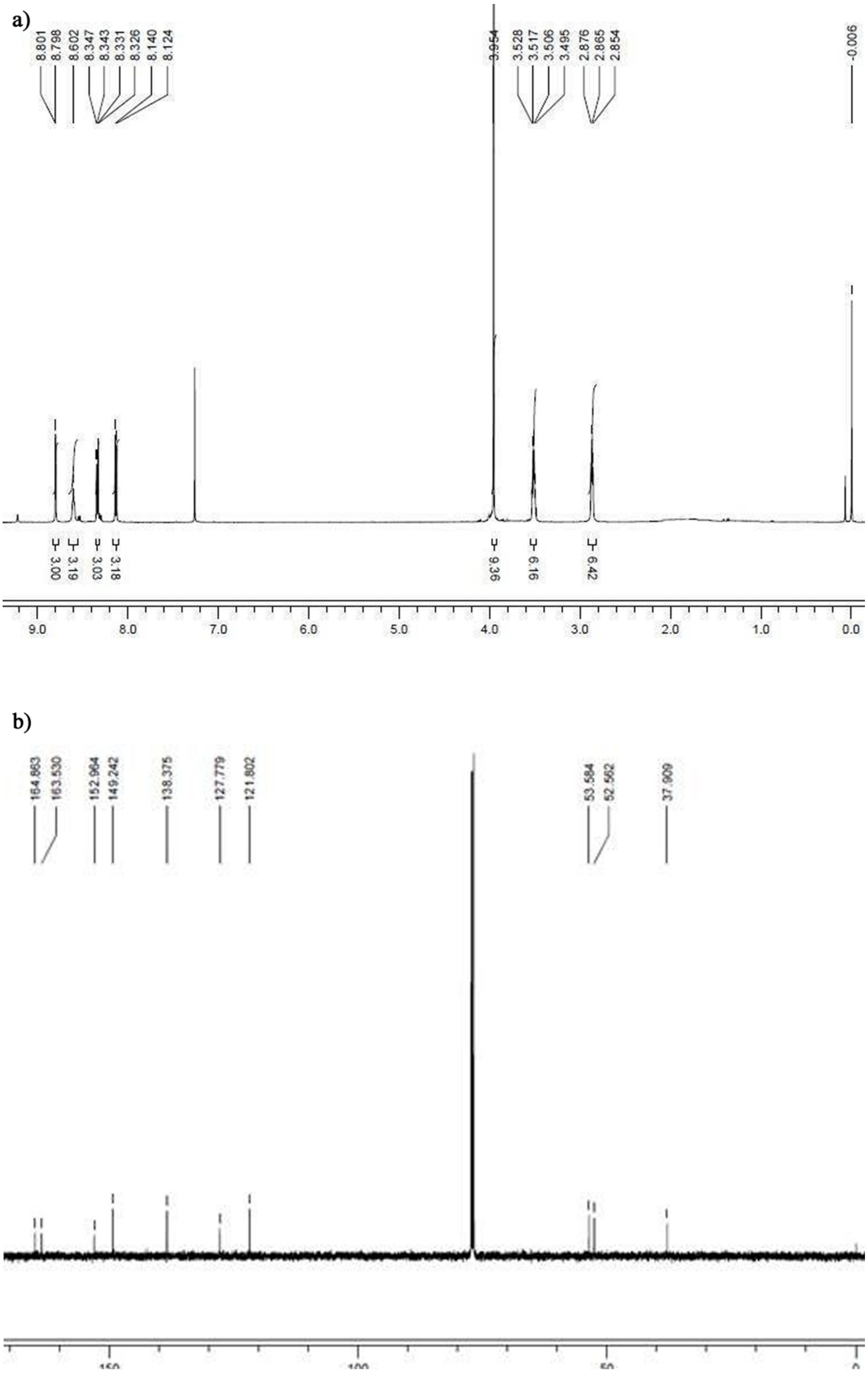
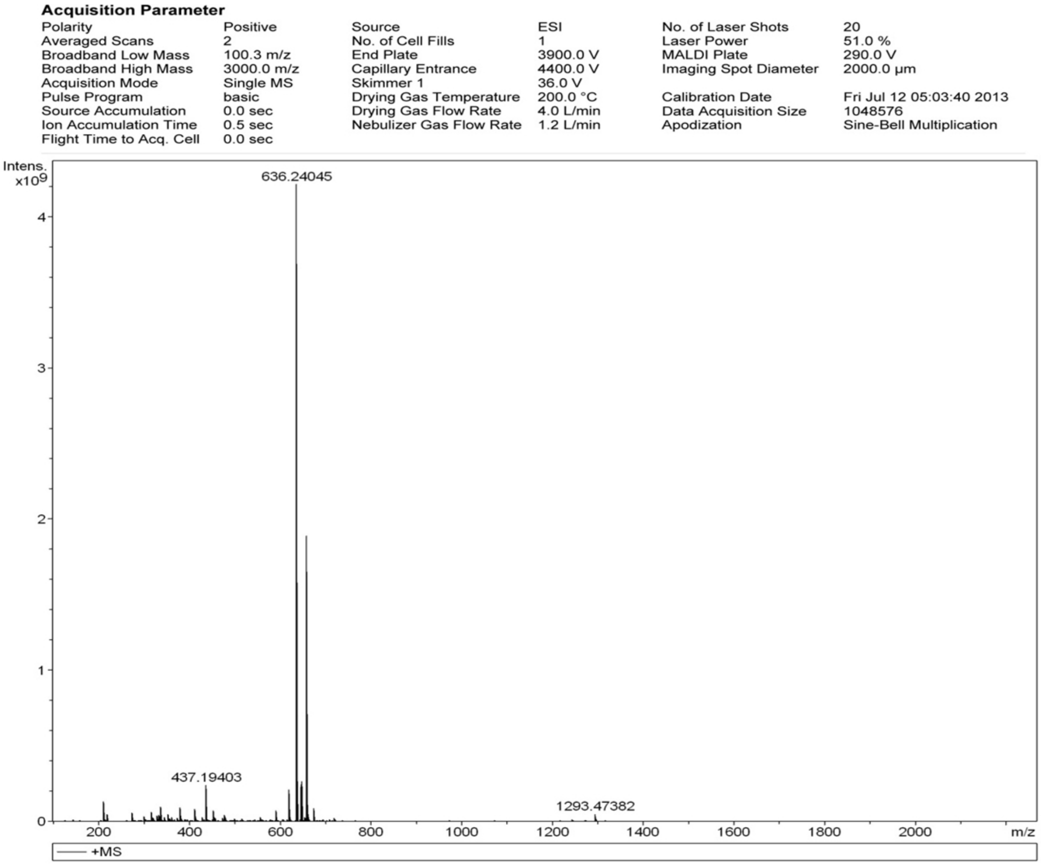


Figure S3. a) ^{1}H NMR spectrum of (**H_3L, 1**) (up); b) ^{13}C NMR spectrum of (**H_3L, 1**) (down).



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Acquisition Parameter
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Averaged Scans           2             No. of Cell Fills         1            Laser Power              51.0 %
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Broadband High Mass      3000.0 m/z    Capillary Entrance        4400.0 V     Imaging Spot Diameter    2000.0 µm
Acquisition Mode         Single MS     Skimmer 1                 36.0 V
Pulse Program            basic         Drying Gas Temperature    200.0 °C     Calibration Date         Fri Jul 12 05:03:40 2013
Source Accumulation      0.0 sec       Drying Gas Flow Rate      4.0 L/min    Data Acquisition Size    1048576
Ion Accumulation Time    0.5 sec       Nebulizer Gas Flow Rate   1.2 L/min    Apodization              Sine-Bell Multiplication
Flight Time to Acq. Cell 0.0 sec
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Figure S4. HR-MS spectrum of the ligand (**H_3L, 1**).

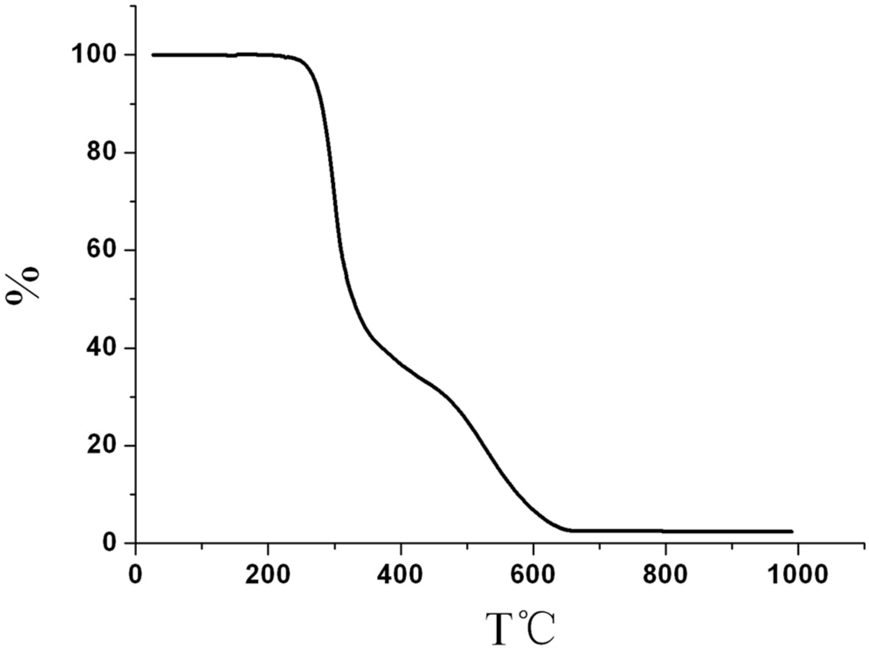

Figure S5. TGA curve of the ligand (**H_3L, 1**).

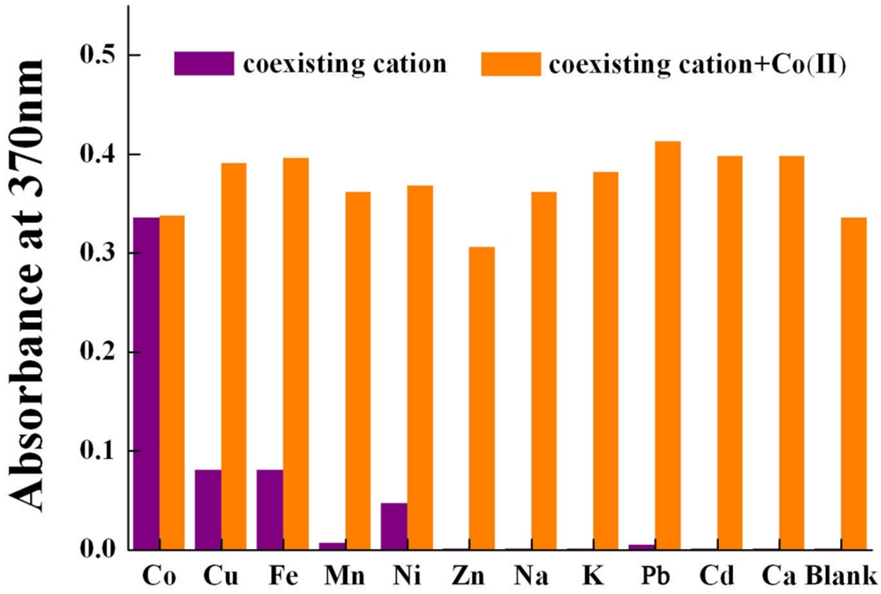

Figure S6. Column chart of the UV-vis absorbance measured at 370 nm of the $\mathbf{H_3L}$ solutions in the presence of different metal ions. (The absorbance of the $\mathbf{H_3L}$ solution was defined as zero, all the metal ions were added as their perchlorate salts, the blank means $\mathbf{H_3L}$ solution, all the metal ions were added equivalent to the H_3L)

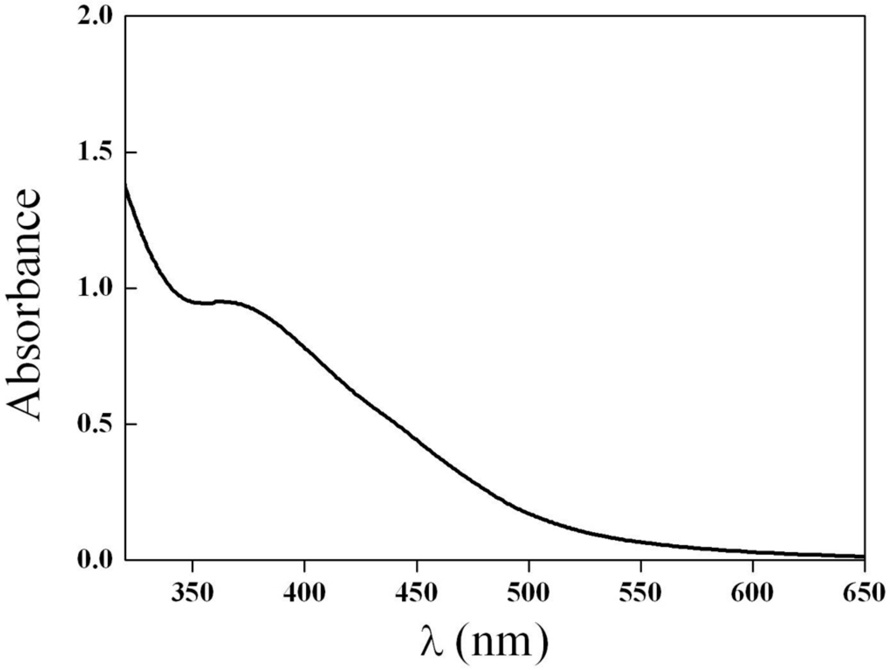

Figure S7. UV-vis spectrum of the aqueous solution of crystal **CoL** at a concentration of 2.46×10^{-4} mol/L. The peak of the spectrum centered at 370 nm. The solution was the same color as it showed in Figure 3 and Figure 8.

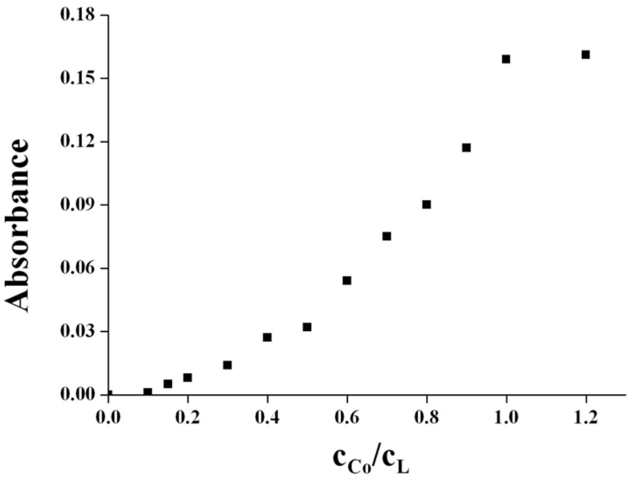

Figure S8. Changes in UV-vis spectrum of **H_3L** in DMSO/H_2O (50/1, v/v) solution (5×10^{-5} mol/L) upon successive addition of Co^{2+} (0-1.2 equiv). The concentration of the Co^{2+} in the solution above is 2.5×10^{-6}, 4.9×10^{-6}, 7.3×10^{-6}, 9.6×10^{-6}, 1.5×10^{-5}, 2.0×10^{-5}, 2.5×10^{-5}, 3.0×10^{-5}, 3.5×10^{-5}, 4.0×10^{-5}, 4.5×10^{-5}, 4.9×10^{-5}, 5.9×10^{-5} mol/L, respectively (The absorbance of the **H_3L** solution was defined as zero, the Co^{2+} was added as its perchlorate salt).

IR spectra

The IR spectrun of **H_4L-NO_3** has a much stronger absorption at 1038 cm^{-1}, which is the specific peak of NO_3^-, and the absorption of 1100 cm^{-1} means there exists ClO_4^- in the complex. The strong absorption at 1655 cm^{-1}means there exists –NH in the **H_3L**, while the amide turned to be –NR in the complexes of **Co-Ac-HL** and **CoL**.

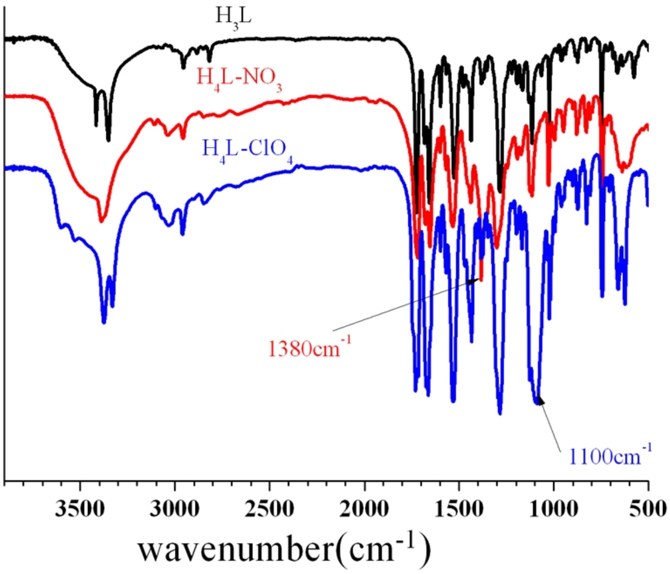

Figure S9. IR spectra of **H_3L**, **H_4L-NO_3**, **H_4L-ClO_4.**

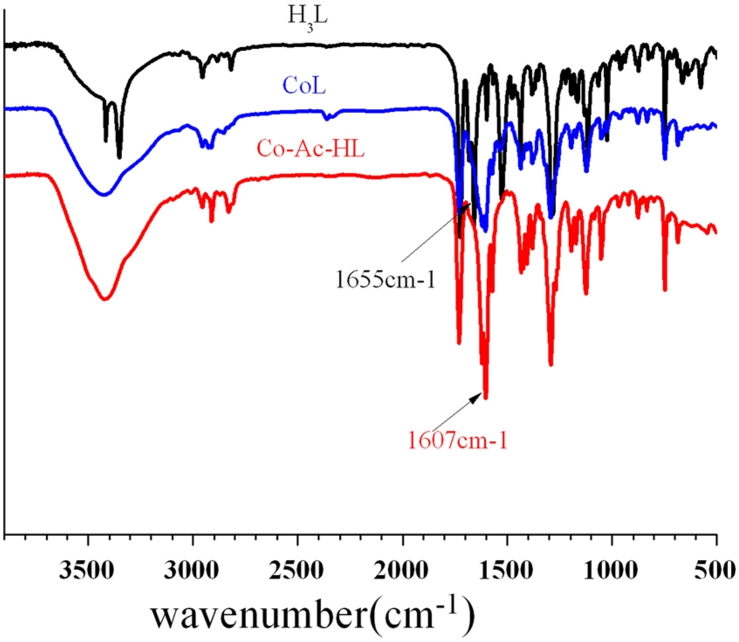

Figure S10. IR spectra of **H_3L**, **Co-Ac-HL**, **CoL**.

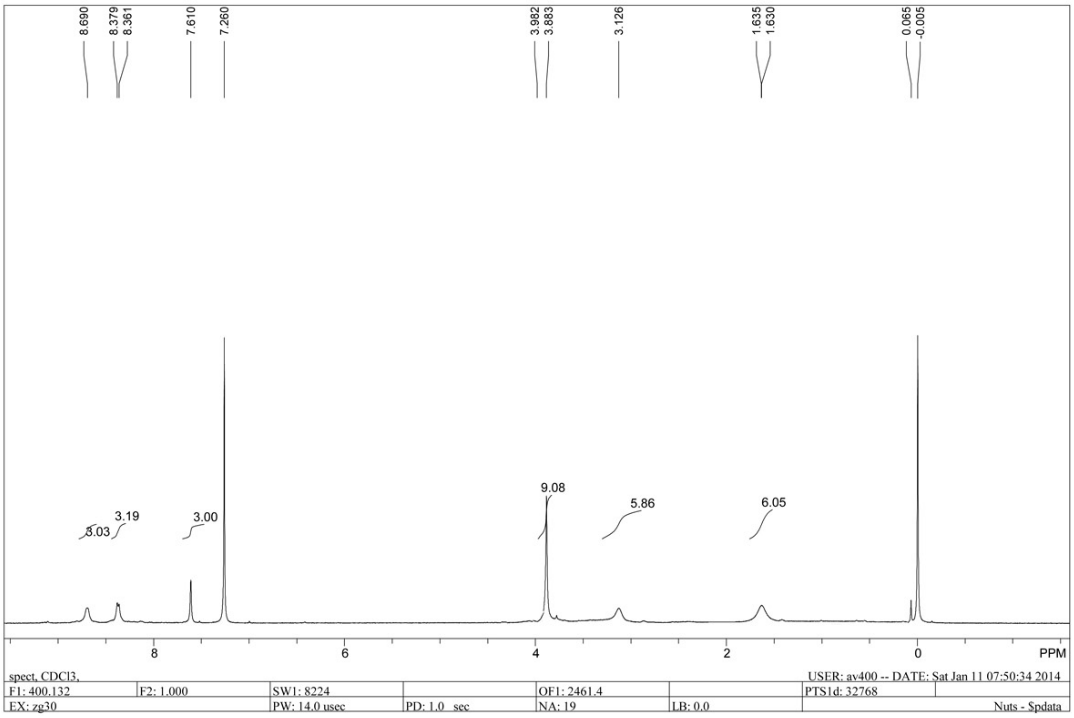

Figure S11. ^1H NMR of (**CoL, 2**). Comparing to the ^1H NMR of **H_3L**, the H of amide $\delta = 8.60$ (s, 3H) disappeared, all the other H experienced considerable highfield shifts, due to the six coordination of the center Co(III).

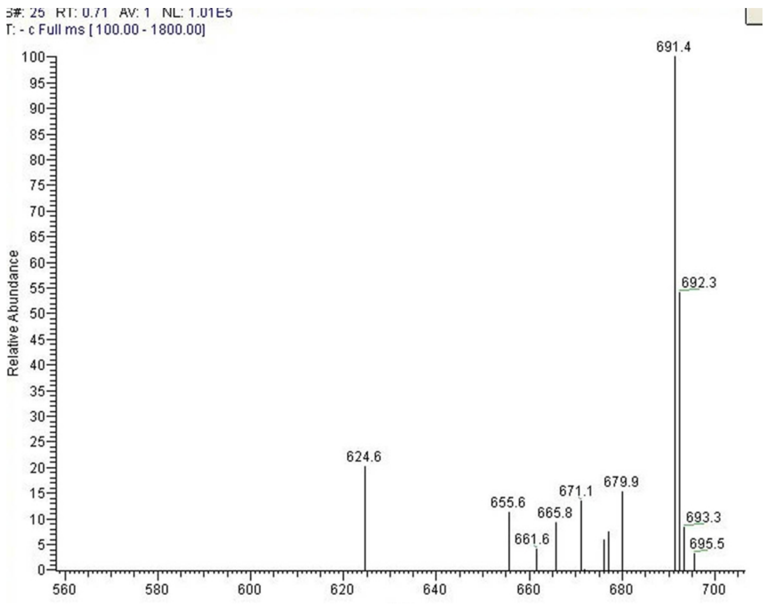

Figure S12. MS spectra of **CoL** (m/z = 691.4).

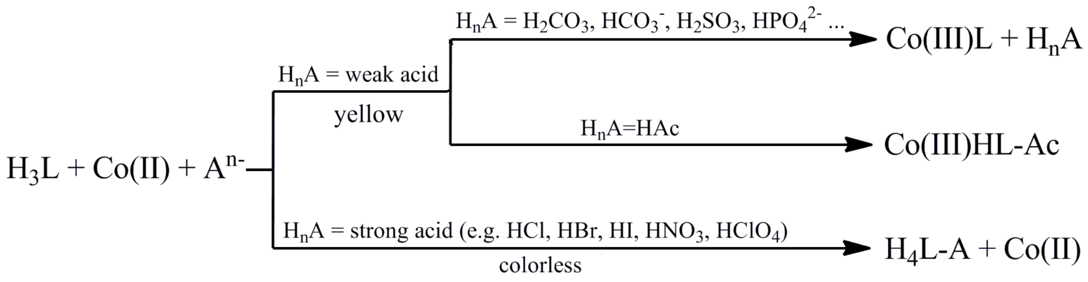

Figure S13. The interation between cobalt (II) salt and **H_3L**.