Supplementary Index

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1. Experimental Details

1.1. Materials and Methods

The ligand (HL) was prepared according to the previous reports.1-3 All other reagents and solvents were obtained from commercial sources without further purification.

Powder X-ray diffraction (PXRD) data were performed on a Rigaku/max 2550 diffractometer with Cu Kα radiation Field-emission (λ = 1.5418 Å, continuous, 40 kV, 40 mA, increment = 0.02°). The elemental analysis (C, H, N) in the solid sample was carried out on a Perkin-Elmer 2400LS II elemental analyzer. TGA (thermal gravimetric analysis) was recorded under an air atmosphere with a heating rate of 10 °C/min using a TGA Q500 V20.10 Build 36 in the temperature range of 35-800 °C. The infrared (IR) spectra were recorded on a Perkin Elmer Spectrum 1 spectrophotometer with KBr pellets within the 4000-400 cm⁻¹ region. Luminescence lifetime was calculated with the Origin 7.5 software package.

1.2 Synthesis of \([\text{EuL}_2(\text{H}_2\text{O})_3]\text{(NO}_3\text{)}\) (EuL)

Eu(NO₃)₃•6H₂O (0.1 mmol, 44.6 mg), and HL (0.3 mmol, 60.1 mg) in a mixed solvent of acetonitrile (CH₃CN, 6 ml) and distilled water (H₂O, 1 ml) were placed in a Teflon-lined stainless steel vessel (20 mL) and heated to 80 °C in 300 min, maintained at this temperature for four days and then cooled to room-temperature at a rate of 0.5 °C/min. The resulting colorless crystals were obtained, after being washed by distilled water, yield ~50 mg (75% based on Eu³⁺). Its purity was confirmed by powder X-ray diffraction (Fig. S3a,b). Elemental analysis (% calc/found) for EuL C₂₂H₂₀EuN₅O₁₀ (Mᵣ = 666.39): C, 39.65/39.70; H, 3.03/2.98; N, 10.51/10.53.

1.3 Single Crystal X-ray structure determination

Single crystal of EuL was selected for indexing and data collection on a Bruker Apex II CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K. Data processing was accomplished with the SAINT program. All absorption corrections were applied using the multi-scan program SADABS.⁴ All structures were solved by direct methods using SHELXS-97 program of the SHELXTL package and refined by the full-matrix least squares method with SHELXTL-97.⁵ All non-hydrogen atoms were easily found from the difference Fourier map and refined using the full-matrix least-squares method on F² with anisotropic thermal parameters during the final cycles. All hydrogen atoms were placed by geometrical considerations and were added to the structure factor calculation. See the CIF file for details. Crystallographic data for EuL is summarized in Table S1. Selected bond distances and angles are given in Table S2.

Table S1 Summary of Crystal Data and Structure Results for EuL.

<table>
<thead>
<tr>
<th>Compound</th>
<th>EuL</th>
</tr>
</thead>
</table>

2
Empirical formula: \( \text{C}_{22}\text{H}_{20}\text{EuN}_{5}\text{O}_{10} \)

Structural formula: \( \{\text{EuL}(\text{H}_2\text{O})_3\}(\text{NO}_3) \) 

\[ \text{fw} = 666.39 \]

Crystal system: Triclinic 
Space group: \( P\overline{1} \)

Temperature (K): 293(2)

\( \lambda (\text{Mo K}\alpha), \text{Å} \): 0.71073

\( a/\text{Å} \): 9.5509(5)

\( b/\text{Å} \): 11.2004(5)

\( c/\text{Å} \): 12.8518(6)

\( \alpha /^\circ \): 66.2700(10)

\( \beta /^\circ \): 76.4140(10)

\( \gamma /^\circ \): 80.5810(10)

\( V/\text{Å}^3 \): 1219.66(10)

\( Z \): 2

2\( \theta \) max (deg): 52.34

\( \mu (\text{Mo-K}\alpha) \text{ mm}^{-1} \): 2.638

\( D, \text{ g/cm}^3 \): 1.815

\( F(000) \): 660

Crystal size (mm\(^3\)): \( 0.35 \times 0.30 \times 0.26 \)

Reflections collected / unique: 7804/4848 [\( R(\text{int}) = 0.0219 \)]

Final \( R \) indices [\( I > 2\sigma(I) \)]: \( a \) \( R_1 = 0.0269, b \) \( wR_2 = 0.0588 \)

\( R \) indices (all data): \( a \) \( R_1 = 0.0314, b \) \( wR_2 = 0.0608 \)

GOF: 1.029

\[ a \) \( R_1 = \sum|F_o| - |F_c|/\sum|F_o|, b \) \( wR_2 = (\sum w[(F_o)^2-(F_c)^2]^2/\sum w(F_o)^2)^{1/2} \)

Table S2. Selected bond lengths and bond angles for EuL.

<p>| Eu(1)-O(1)   | 2.510(2) | Eu(1)-O(2)   | 2.435(2) |</p>
<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
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<tr>
<td>Eu(1)-O(3)</td>
<td>2.384(2)</td>
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<tr>
<td>Eu(1)-O(5)</td>
<td>2.513(3)</td>
<td></td>
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<tr>
<td>Eu(1)-O(1W)</td>
<td>2.436(2)</td>
<td></td>
</tr>
<tr>
<td>Eu(1)-O(3W)</td>
<td>2.436(2)</td>
<td></td>
</tr>
<tr>
<td>O(1)-Eu(1)-O(6)</td>
<td>69.78(8)</td>
<td></td>
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<tr>
<td>O(1)-Eu(1)-N(5)</td>
<td>90.13(8)</td>
<td></td>
</tr>
<tr>
<td>O(2)-Eu(1)-O(5)</td>
<td>127.61(8)</td>
<td></td>
</tr>
<tr>
<td>O(2)-Eu(1)-O(3W)</td>
<td>127.35(8)</td>
<td></td>
</tr>
<tr>
<td>O(2)-Eu(1)-O(1W)</td>
<td>87.38(9)</td>
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<tr>
<td>O(3)-Eu(1)-O(4)#1</td>
<td>87.98(7)</td>
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<tr>
<td>O(3)-Eu(1)-O(2)</td>
<td>149.18(9)</td>
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<td>O(3)-Eu(1)-O(3W)</td>
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<tr>
<td>O(3)-Eu(1)-N(5)</td>
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<td>O(4)#1-Eu(1)-O(5)</td>
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<td>O(6)-Eu(1)-N(5)</td>
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<td>O(1W)-Eu(1)-O(3W)</td>
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<td>O(1W)-Eu(1)-O(1)</td>
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<td>O(2W)-Eu(1)-O(2)</td>
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<td>O(2W)-Eu(1)-N(5)</td>
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<td>O(3W)-Eu(1)-O(1)</td>
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<tr>
<td>O(3W)-Eu(1)-O(6)</td>
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**Hydrogen bonds**

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1W)-H(1WA)...N(2)#2</td>
<td>0.85</td>
<td>2.836(4)</td>
<td>135.1</td>
</tr>
<tr>
<td>O(2W)-H(2WB)...O(4)</td>
<td>0.85</td>
<td>2.759(3)</td>
<td>156.8</td>
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<tr>
<td>O(2W)-H(2WA)...N(1)#3</td>
<td>0.85</td>
<td>2.763(4)</td>
<td>129.7</td>
</tr>
<tr>
<td>O(3W)-H(3WA)...O(1)#4</td>
<td>0.85</td>
<td>2.720(3)</td>
<td>140.4</td>
</tr>
<tr>
<td>O(3W)-H(3WB)...N(3)#5</td>
<td>0.85</td>
<td>2.887(4)</td>
<td>154.7</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z+1; #2 x, y-1, z+1; #3 -x+2, -y+1, -z; #4 -x+1, -y+1, -z+1; #5 -x, -y, -z+2.

2. Structural images
Fig. S1 (a) ORTEP representation of the asymmetric unit of EuL. Thermal ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are omitted for clarity. (b) Coordination mode and its polyhedron of Eu1. (b) The dihedral angles between phenyl and pyrimidine rings, calculated with SHELXTL-97 program.
Fig. S2 (a-d) The H-bonded one-dimensional (1D) chains along different directions among coordinated water molecules (O(1W), O(2W), and O(3W)) as well as non-coordinated N sites (N(1), N(2), and N(3)) and oxygen atom (O(1)) of carboxylate group. (e) A H-bonded 3D framework viewed along the [010] direction. EuO₆ polyhedra are shaded in green. Hydrogen bonds are drawn as dashed lines (red).

3. Powder X-ray diffraction, FTIR, and thermogravimetric analyses:

3.1 PXRD analyses

All Powder X-ray diffraction (PXRD) patterns containing as-made EuL and samples after immersing various solvents were performed on a Rigaku/max 2550 diffractometer with graphite-filtered Cu Kα radiation Field-emission (\(\lambda = 1.5418 \text{ Å}\)) at 40 kV and 40 mA. The spectra were collected in the range of 5-60° (2\(\theta\)) at a scan speed of 5 deg/min.

As shown in Fig. S3a and b, the measured PXRD patterns of EuL match well with the simulated pattern generated from the result of single-crystal diffraction data, confirming the phase purity of as-synthesized product.

In order to demonstrate the thermal stability of EuL, its temperature-dependent powder X-ray diffraction patterns (Fig. S3c) are recorded on a PANalytical diffractometer with Cu Kα radiation Field-emission (\(\lambda = 1.5418 \text{ Å}\), continuous, 40 kV, 30 mA, increment = 0.02°) at 25 °C, 30 °C, 100 °C, 150 °C, 250 °C, 350 °C, 400 °C and 500 °C, respectively, which is accordant with the inflection points of TGA curve. The results show that the framework of EuL is thermally stable till 350 °C.

EuL samples are insoluble in various common solvents containing water solution. In order to determine the solvent-stability of EuL treated by different solvents, the samples of EuL/solvents were prepared by introducing each sample (30 mg) as a powder into different solvents (ethanol, 1-prapanol (1-PA), 2-propanol (2-PA), acetonitrile (CH₃CN), dichloromethane (CH₂Cl₂), aniline, and H₂O) and then agitated for 48 h. After treatment, the powder was obtained by filtration, and drying in the air. The obtained PXRD patterns are shown in Figure S3d. It is clear that the basic frameworks of the compound remain intact after immersing in solvent molecules and illustrate good solvent-stability.

Before researching the quenching behavior of various amines in detail, such as ammonium hydroxide (NH₃·H₂O, 25%~28%), methylamine (CH₃NH₂, 25%~30%), ethylamine (C₂H₅NH₂, 65%~70%), propylamine (C₃H₇NH₂, 98.5%), N,N’-diethylamine ((C₂H₅)₂NH, analytical reagent), triethylamine ((C₂H₅)₃N, analytical reagent), and aniline (analytical reagent), the stabilities of EuL introduced by various amine solvents have been also demonstrated by PXRD, as shown in Fig. S3e.
3.2 IR analyses

IR peaks (cm\(^{-1}\)) for \textit{EuL}: 3403 (s), 3066 (w), 3041 (w), 2426 (w), 1642 (w), 1589 (m), 1529 (m), 1468 (w), 1408 (m), 1381 (s), 1300 (s), 1185 (m), 1125 (w), 1103 (w), 1033 (w), 1006 (w), 918 (w), 859 (w), 815 (w), 793 (m), 717 (m), 690 (w), 651 (w), 543 (w), 482 (w).

IR peaks (cm\(^{-1}\)) for \textit{HL}: 3080 (w), 3038 (w), 2927 (w), 2778 (w), 2604 (w), 2497 (w), 1914 (m), 1719 (s), 1613 (m), 1554 (m), 1512 (m), 1412 (s), 1359 (w), 1284 (s), 1190 (s), 1104 (m), 972 (w), 919 (m), 856 (s), 803 (w), 765 (vs), 718 (m), 697 (m), 654 (m), 549 (m), 523 (m).

IR peaks (cm\(^{-1}\)) for \textit{EuL/1-propanol}: 3297 (s), 1587 (m), 1528 (m), 1470 (m), 1412 (s), 1300 (s), 1184 (m), 1036 (m), 1004 (m), 919 (w), 856 (m), 813 (w), 793 (m), 718 (m), 686 (w), 649 (w), 538 (m).

IR peaks (cm\(^{-1}\)) for \textit{EuL/2-propanol}: 3292 (s), 1587 (m), 1534 (m), 1465 (m), 1407 (s), 1300 (s), 1190 (m), 1126 (w), 1036 (m), 1004 (m), 919 (w), 861 (s), 819 (w), 792 (s), 718 (m), 686 (w), 654 (m), 538 (w).

IR peaks (cm\(^{-1}\)) for \textit{EuL/ethanol}: 3287 (s), 1592 (m), 1534 (m), 1465 (w), 1406 (s),
1295 (m), 1190 (m), 1126 (w), 1105 (w), 1036 (w), 1004 (m), 919 (w), 861 (m), 813 (w), 787 (m), 718 (m), 680 (w), 649 (w), 543 (m).

IR peaks (cm\(^{-1}\)) for \(\text{EuL/aniline}\): 3529 (w), 3288 (m), 3065 (w), 3033 (w), 1646 (w), 1603 (w), 1587 (m), 1529 (m), 1471 (m), 1408 (s), 1301 (m), 1190 (m), 1121 (w), 1106 (w), 1031 (w), 919 (w), 857 (m), 814 (w), 788 (m), 724 (m), 687 (w), 645 (w), 539 (w).

IR peaks (cm\(^{-1}\)) for \(\text{EuL/CH}_2\text{Cl}_2\): 3271 (m), 3068 (w), 1645 (w), 1608 (m), 1592 (m), 1534 (m), 1470 (m), 1412 (vs), 1343 (w), 1300 (s), 1184 (m), 1126 (w), 1105 (w), 1052 (w), 1036 (m), 1004 (m), 919 (w), 856 (m), 813 (w), 787 (m), 718 (m), 686 (w), 649 (w), 543 (w).

IR peaks (cm\(^{-1}\)) for \(\text{EuL/CH}_3\text{CN}\): 3276 (m), 3065 (w), 3038 (w), 1645 (w), 1608 (w), 1586 (m), 1534 (m), 1465 (m), 1407 (vs), 1300 (s), 1184 (m), 1126 (w), 1105 (w), 1036 (w), 1009 (w), 919 (w), 856 (m), 813 (w), 792 (m), 723 (m), 686 (w), 849 (w), 543 (w).

As shown in Fig. S4b-g, these infrared spectra also confirm that the framework of \(\text{EuL}\) is retained after the introduction of various solvents, and each of them shows slightly changes for position and intensity of absorption bands, confirming the successful incorporation of guest molecules during the immersing process.

Take \(\text{EuL/aniline}\) as an example (Fig. S4e), the absorption band at about 1300 cm\(^{-1}\) clearly strengthen than the one of \(\text{EuL}\), which are attributed to the characteristic stretching vibration of C-N. Besides, the shift of the \(\nu (\text{O-H})\) band of coordinated water molecules from 3403 to 3288 cm\(^{-1}\) and one new \(\nu (\text{N-H})\) band at 3529 cm\(^{-1}\) indicate the formation of hydrogen bonds between aniline and coordinated water molecules of \(\text{EuL}\) framework.

As shown in Fig. 4i, the framework of \(\text{EuL}\) after heating at 200 °C is retained, and coordinated water molecules have been released, since the adsorption band at 3403 cm\(^{-1}\), coming from the vibration of \(\nu (\text{H}_2\text{O})\) band, became very weak.
Fig. S4 The IR spectra of EuL (a), and EuL immersed in different solvents, namely, EuL/1-propanol (b), EuL/2-propanol (c), EuL/ethanol (d), EuL/aniline (e), EuL/CH₂Cl₂ (f), EuL/CH₃CN (g), as well as contrastive spectra between EuL and EuL/aniline (h), and IR spectra of EuL after heating 150 °C, and 200 °C for one hour (i).

3.3 TGA analysis

Fig. S5 TGA-DTA curves of EuL under air atmosphere with a heating rate of 10 °C/min.

As shown in Fig. S5, the TGA curve displays three continuous weight losses of 8.0% (calculated 8.1%) at 120-231 °C corresponding to the loss of three coordinated water molecules. The dehydrated framework is stable to 395 °C, then the framework begins to collapse, accompanying the release of organic ligands (two {L}⁻ ligands) and one nitrate ion. The total weight loss at 504 °C is 59.6%. So, this compound EuL has a certain thermal stability, which has been also verified by the FTIR spectra (Fig. S4i) and PXRD patterns (Fig. 3c) at different temperatures.

4. Photoluminescent Properties

The fluorescent property of EuL was investigated in the solid state, in various solvent emulsions and vapors at room temperature.

4.1 Solid-state spectra

The photoluminescent spectra of EuL and HL in the solid state were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The photomultiplier tube (PMT) voltage was 700 V, the scan speed was 1200 nm min⁻¹ and the slit width of excitation and emission was 2.5 nm and 5.0 nm, respectively.
Fig. S6 Room-temperature excitation (black) and emission spectra (red) of ligand HL ($\lambda_{em} = 349$ nm and $\lambda_{ex} = 237$ nm) as well as complex EuL ($\lambda_{em} = 620$ nm and $\lambda_{ex} = 308$ nm).

4.2 Sensing for organic solvent molecules in the liquid

The photoluminescent (PL) spectra of EuL in various solvent emulsions at room temperature were recorded on a Hitachi F-7000 fluorescence spectrophotometer, a LS 55 fluorescence spectrophotometer, and a Hitachi F-4500 fluorescence spectrophotometer, respectively. The photomultiplier tube (PMT) voltage was 700 V and the PMT slit width of excitation and emission was 2.5 nm, respectively. The EuL-solvent emulsions were prepared by introducing 5 mg of its powder into 3.0 mL of methanol, ethanol, 1-propanol, 2-propanol, acetonitrile (CH$_3$CN), chloroform (CHCl$_3$), dichloromethane (CH$_2$Cl$_2$), tetrahydrofuran (THF), N,N-Dimethylformamide (DMF), benzene, toluene, aniline, chlorobenzene, H$_2$O, and were then vigorously agitated by using ultrasound to form stable emulsions before fluorescence study. For sensing properties with respect to aniline, different amounts of aniline were added into a standard EuL emulsion in 2-propanol, while the concentration of the Eu$^{3+}$ ions was kept constant.
Fig. S7 The room-temperature photoluminescence spectra of EuL in different solvents with excited at 308 nm (top), and the amplifying image (down).

Fig. S8 (a) Luminescence quenching of EuL/2-propanol emulsion with increasing aniline content (μL) (λex =308 nm). (b) The emission intensity of the 5D0→7F2 transition (620 nm) for EuL/2-propanol emulsion as function of aniline content (μL).

Fig. S9 (a) Suspension-state PL spectra and (b) the relative intensities of 5D0→7F2
transition at 620 nm for **EuL** dispersed in various amine solvents (3 mL) when excited at 308 nm, such as NH₃•H₂O, CH₃NH₂, C₂H₅NH₂, C₃H₇NH₂, (C₂H₅)₂NH, and (C₂H₅)₃N.

![Spectra of EuL/2-propanol emulsion](image1)

![Spectra of EuL/2-propanol emulsion](image2)

![Spectra of EuL/2-propanol emulsion](image3)

![Spectra of EuL/2-propanol emulsion](image4)

**Fig. S10** Spectra of EuL/2-propanol emulsion in the presence of different amounts of other amines (NH₃•H₂O, CH₃NH₂, C₂H₅NH₂, C₃H₇NH₂, (C₂H₅)₂NH, and (C₂H₅)₃N) (λₑx = 308 nm).

**4.3 Sensing for various amines vapors**

The synthesized sample was ground and used for vapor sensing experiments. For each experiment, 30 mg of EuL was placed into a glass tube (5 mL), then exposure to various amines vapors for 24 h. Subsequently the sample tube was taken out of the container, quickly sealed and the emission spectra were measured in the solid sample.
holder. The experimental set-up is depicted in Fig. S11.

Fig. S11 Diagram of gas-sensing measurements for amines vapors.

Fig. S12 (a) The luminescence spectra of EuL after incubated for 24h under various amine vapors when excited at 308 nm; (b) the related luminescence intensity of the $^5D_0 \rightarrow ^7F_2$ transition (620 nm).

In order to test the response rate of EuL for each amine vapor, the time-dependent fluorescence quenching profile need to be obtained. Design a new experimental sensor setup to measure solid-state photoluminescence in various
amine vapors, as shown in Fig. S13. Solid samples of EuL (60 mg) were ground into powder, which is further pressed into firm sheet sample. A quartz slide was carved into the dimensions 0.7 cm × 1.5 cm, equal to the diagonal distance of suprasil cuvette. The firm sheet sample sticks to the quartz slide through a double-sided black conductive adhesive, far from the bottom side about 1.2 cm. Any excess samples are removed by gently scraping the edges of the sheet sample with a drawknife in order to be placed readily into a cuvette (1.0 cm). The cuvette containing the sensor slide is positioned on the universal solid sample holder, existing in the Hitachi F-4500 spectrophotometer, and adjusted to a suitable position. The solid state emission spectrum of firm sheet sample is carried out and as an original standard, then different amines solution ~150 μL are added into the cuvette by toppette pipettor. Caution! To eliminate the measurement errors, the cuvette must be kept still, so the toppette pipettor does not touch with cuvette during adding solution. Then the cap is carefully put on the cuvette. The luminescence spectra and intensity as well as the response rate of the sensor slide versus time plots were obtained in different amine vapors.

As shown in Fig. S13, the length and width are 1 cm, the height is 2 cm for the cuvette used, so its volume is 2 cm³. The amines solution about 150 μL is added into it. Take aniline as an example, the concentration of aniline in the cuvette is 7.13 mmol/cm³, if the 150 μL solution of aniline is fully vaporized. But in fact, the concentration of target vapor is difficultly measured in the cuvette because the saturate vapor pressure of each analyte is different.

Fig. S13 Designed sensor setup used for the solid-state photoluminescence measurements as a function of time in different amine vapors.
5. The mechanism of luminescent response

Fig. S14 Emission spectra of EuL upon exposure to different amine vapors at various time intervals at room temperature ($\lambda_{ex} = 308$ nm). ‘s’ stands for ‘second’, and ‘min’ stands for ‘minute’.
UV–vis spectroscopic studies were collected on a UV-2450 spectrophotometer to deeply understand the luminescent response.

![UV absorption spectra](image)

Fig. S15 UV absorption spectra of EuL and ligand HL (a) as well as various solvents (b) and target different amines (c) in ethanol.

**References:**


4. G. M. Sheldrick, SADABS; University of Göttingen: Germany, 1996.

5. (a) G. M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Determination; University of Göttingen: Germany, 1997; (b) G. M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement; University of Göttingen: Germany, 1997; (c) CrystalClear, version 1.3.5; Rigaku Corp.: Woodlands,