

# Transition metal ion induced hydrogelation by amino-terpyridine ligands

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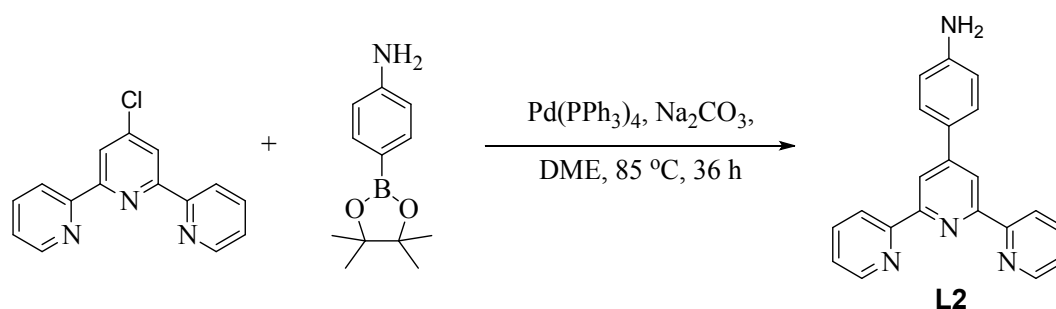
## Experimental Section

**General information and Materials:** Unless stated otherwise, all reagents and solvents were purchased from Aldrich chemicals and used without further purification. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Avance III HD 300 and DRX 400 NMR spectrometer. Chemical shifts were expressed in ppm. Mass spectra were measured on a Micromas (ESI-TOF) spectrometer. SEM images were obtained on Bruker Quantax400 EDS (Zeiss EVO-50XVP), while TEM images were recorded on JEOL JEM-1400HC at 80 kV. The crystal structure of ZnCl<sub>2</sub>(L1) was previously reported in our published article.<sup>1</sup>

### Synthesis of 4'-(4-N,N'-dimethylaminophenyl)-2,2':6',2''-terpyridine (L1)

The ligand 4'-(4-N,N'-dimethylaminophenyl)-2,2':6',2''-terpyridine **L** was synthesized according to the literature method.<sup>2</sup> 2-Acetylpyridine (4.84 g, 40 mmol) was added to a solution of 4-dimethylaminobenzaldehyde (3 g, 20 mmol) in ethanol (100 mL). KOH pellets (3.4 g, 85%, 51 mmol) and aq. NH<sub>3</sub> (58 mL) were added to the stirred solution and the resulting mixture was stirred at room temperature for 30 h. The precipitate was then filtered, washed several times with ethanol. The precipitate was then dissolved in chloroform (10 mL) and excess *n*-hexane added (50 mL). The greenish solid was filtered, washed with *n*-hexane and dried in air. Yield 2.2 g (6.2 mmol, 31%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ/ppm: 8.73-8.75 (m, 2H), 8.72 (s, 2H), 8.66 (dt, 2H, *J* 8.0 Hz, 1.1 Hz), 7.84-7.90 (m, 4H), 7.31-7.35 (m, 2H), 6.82 (dt, 2H, *J* 9.0 Hz, 2.0 Hz), 3.04 (s, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ/ppm: 156.7, 155.7, 151.1, 150.0, 149.0, 136.8, 128.1, 125.6, 123.6, 121.4, 117.6, 112.3, 40.4. HRMS (ESI-TOF) *m/z* calcd for [M+H]<sup>+</sup> (C<sub>23</sub>H<sub>21</sub>N<sub>4</sub>)<sup>+</sup>: 353.17607; found: 353.1774.

## Synthesis of 4'-(4-aminophenyl)-2,2':6',2''-terpyridine (L2)



4'-Chloro-2,2':6',2''-terpyridine (401 mg, 1.5 mmol), 4-aminophenylboronic acid pinacol ester (396 mg, 1.81 mmol, 1.2 equiv.) and dimethoxyethane (25 mL) were placed in an oven-dried Schlenk tube and the solution was degassed and then placed under argon. Sodium carbonate (480 mg, 4.53 mmol, 3.0 equiv.) was dissolved in water (6 mL) water in a separate Schlenk and degassed similarly. The catalyst, [Pd(PPh<sub>3</sub>)<sub>4</sub>] (107 mg, 0.093 mmol, 0.062 equiv.) was added to the first Schlenk, followed immediately by the sodium carbonate solution. After stirring the solution at room temperature for 1 h, the temperature was increased to 85 °C for 36 h. After cooling down, the solution was diluted with dichloromethane and filtered over celite. The filtrate washed with saturated NH<sub>4</sub>Cl, brine, dried (MgSO<sub>4</sub>) and evaporated to get the crude product. The crude product was purified by column chromatography using chloroform as eluent and recrystallized from boiling ethanol solution. Yield 68%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 8.72–8.74 (m, 2H), 8.69 (s, 2H), 8.66 (d, 2H, *J* 8.0 Hz), 7.87 (td, 2H, *J* 1.7, 7.7 Hz), 7.78 (dt, 2H, *J* 2.0, 8.5 Hz), 7.32–7.36 (m, 2H), 6.80 (dt, 2H, *J* 2.1 8.5Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ/ppm: 156.7, 155.9, 150.1, 149.2, 147.7, 137.0, 128.6, 128.4, 123.8, 121.5, 118.0, 115.4. HRMS (ESI-TOF) *m/z* calcd for [M+H]<sup>+</sup> (C<sub>21</sub>H<sub>17</sub>N<sub>4</sub>)<sup>+</sup>: 325,1448; found: 325.1423.

**Gelation studies of with MCl<sub>2</sub> salts:** To a stock solution of L1/L2 (200 μL, 16 mM in 0.15 N HCl) taken in a test tube (0.5 cm diameter), 200 μL of MCl<sub>2</sub> (16 mM in H<sub>2</sub>O) was added and shaken gently [M= Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup>]. Hydrogels were formed instantaneously.

**Anionic effects on the gelation studies of L1 and L2:** To stock solutions of L1 and L2 (200 μL, 16 mM dissolved individually into 0.15 N HCl, HBr, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HClO<sub>4</sub>, *p*-toluenesulfonic acid, CF<sub>3</sub>SO<sub>3</sub>H and CH<sub>3</sub>SO<sub>3</sub>H) taken in a test tube (0.5 cm diameter), 200 μL of M(ClO<sub>4</sub>)<sub>2</sub> (16 mM in H<sub>2</sub>O) was added to and shaken gently [M= Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup>].

**N.B:** The ligands were generally soluble in 0.15 N acids at room temperature. However, in some cases mild heating and sonication were required. As the normality was kept constant to maintain the acid strength, gelation experiments with H<sub>2</sub>SO<sub>4</sub> solutions of **L1** and **L2** were done in presence of 0.075 M Na<sub>2</sub>SO<sub>4</sub> to balance the SO<sub>4</sub><sup>2-</sup> concentration. Metal perchlorates were chosen to ensure uniform solubility.

**Gelation studies of L1 with Cu(II) in presence of chloride ion:** To stock solutions of **L1** (200 μL, 16 mM dissolved individually into 0.15 N HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HBr, HClO<sub>4</sub> and *p*-toluenesulfonic acid) taken in a test tube (0.5 cm diameter), 100 μL of NaCl solution (32 mM in H<sub>2</sub>O) was added. 100 μL of Cu(ClO<sub>4</sub>)<sub>2</sub> · 6 H<sub>2</sub>O (32 mM in H<sub>2</sub>O) was added to the mixture subsequently and gently shaken. Hydrogels were formed instantaneously.

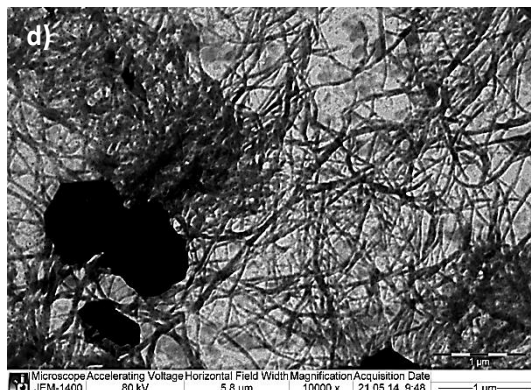
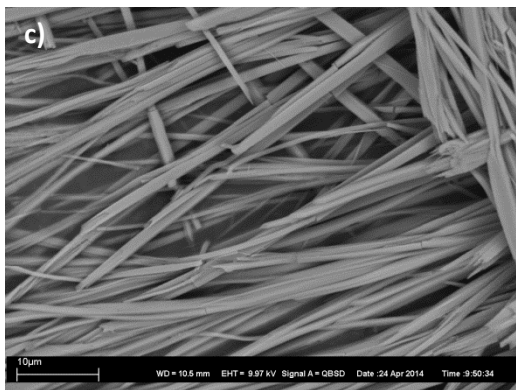
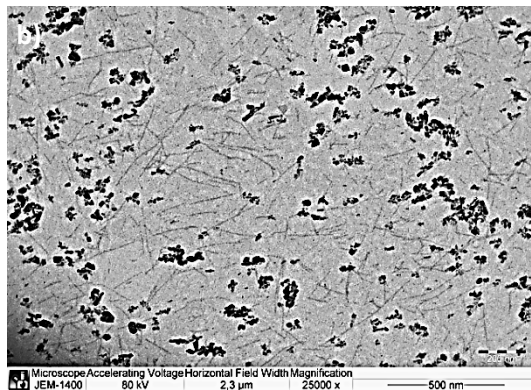
**X-ray crystallographic study:** Diffraction data for all the complexes of **L1** and **L2** were collected on an Agilent SuperNova Dual diffractometer equipped with an Atlas detector. *CrysAlis<sup>PRO</sup>* program was used for data collection and processing.<sup>3</sup> The intensities were corrected for absorption using Analytical face index absorption correction method.<sup>4</sup> The structures were solved with the program *Superflip*<sup>5</sup> and refined by full-matrix least squares on F<sup>2</sup> using the *WinGX* software<sup>6</sup> equipped with *SHELXL-97*.<sup>7</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters. The N-H hydrogens were found from electron density maps and refined by setting U<sub>iso</sub> (H) factors as 1.2 (N-H) times the parent atom factor. All other hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. The unit cell of CdCl<sub>2</sub>(**L1**) includes highly disordered solvent molecules, which could not be modeled as discrete atomic sites. So the structure was subjected to the *SQUEEZE* procedure from the *PLATON* suite to calculate the diffraction contribution of the solvent molecules and thereby produce a set of solvent-free diffraction intensities.<sup>8</sup> Prior to *SQUEEZE*, all non-hydrogen atoms were made anisotropic and all hydrogen atoms were inserted at their calculated positions. Details of the *SQUEEZE* procedure are given in the CIF file. The figures were drawn using the program *Mercury v3.3*.<sup>9</sup>

**Table S1** Crystallographic data and structure refinement parameters for the complexes of **L1**

	CuCl <sub>2</sub> ( <b>L1</b> )	CdCl <sub>2</sub> ( <b>L1</b> )
CCDC number	1021539	1021540
empirical formula	C <sub>26</sub> H <sub>27</sub> Cl <sub>2</sub> CuN <sub>5</sub> O	C <sub>23</sub> H <sub>20</sub> CdCl <sub>2</sub> N <sub>4</sub>
<i>M<sub>w</sub></i> /g	559.96	535.73
<i>T</i> /K	123.01(10)	173.01(10)
$\lambda$ /Å	1.54184	0.71073
crystal color, shape	red, block	yellow, block
crystal size/mm <sup>3</sup>	0.24 x 0.08 x 0.06	0.24 x 0.10 x 0.07
crystal system	triclinic	Orthorhombic
space group	<i>P</i> -1	<i>P</i> na
<i>a</i> /Å	9.5245(6)	27.5775(9)
<i>b</i> /Å	10.9766(6)	27.9449(10)
<i>c</i> /Å	13.0812(3)	10.4795(4)
$\alpha$ /°	66.231(5)	90
$\beta$ /°	83.209(5)	90
$\gamma$ /°	83.846(5)	90
<i>V</i> /Å <sup>3</sup>	1240.15(12)	8076.0(5)
<i>Z</i>	2	12
$\rho_c$ /gcm <sup>-3</sup>	1.500	1.322
$\mu$ /mm <sup>-1</sup>	3.463	1.024
<i>F</i> (000)	578	3216
$\theta$ range/°	3.70 to 67.49	2.08 to 25.00
completeness to $\theta_{full}$	99.5%	99.8 %
reflections collected	8013	7112
independent reflections	8013 [R(int) = 0.0352]	7112 [R(int) = 0.0362]
absorption correction	analytical	Analytical
max. and min. transmission	0.856, 0.639	0.927, 0.886
data/restraints/parameters	8013 / 0 / 320	7112 / 0 / 412
goodness-of-fit on <i>F</i> <sup>2</sup>	0.987	0.975
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0978	R1 = 0.0487, wR2 = 0.1309
R indices (all data)	R1 = 0.0419, wR2 = 0.0996	R1 = 0.0752, wR2 = 0.1438
largest diff. peak and hole (eÅ <sup>-3</sup> )	0.441, -0.349	0.680, -0.474

**Table S2** Crystallographic data and structure refinement parameters for the complexes of **L2**

	ZnCl <sub>2</sub> (L2)	CdCl <sub>2</sub> (L2)	HgCl <sub>2</sub> (L2)
CCDC number	1021541	1021542	1021543
empirical formula	C <sub>21</sub> H <sub>16</sub> Cl <sub>2</sub> N <sub>4</sub> Zn	C <sub>21</sub> H <sub>16</sub> CdCl <sub>2</sub> N <sub>4</sub>	C <sub>21</sub> H <sub>16</sub> Cl <sub>2</sub> HgN <sub>4</sub>
<i>M<sub>w</sub></i> /g	460.65	507.68	595.87
<i>T</i> /K	123.01(10)	123.01(10)	173.01(10)
$\lambda$ /Å	1.54184	1.54184	0.71073
crystal color, shape	yellow, needle	yellow, needle	red, block
crystal size/mm <sup>3</sup>	0.12 x 0.09 x 0.06	0.09 x 0.06 x 0.04	0.54 x 0.26 x 0.15
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	12.5240(3)	12.9203(2)	12.9410(3)
<i>b</i> /Å	9.51563(11)	9.79833(13)	9.8715(2)
<i>c</i> /Å	16.6958(3)	16.0669(3)	16.0933(4)
$\alpha$ /°	90	90	90
$\beta$ /°	108.4790(19)	107.2044(19)	107.168(3)
$\gamma$ /°	90	90	90
<i>V</i> /Å <sup>3</sup>	1887.11(5)	1943.01(6)	1964.27(8)
<i>Z</i>	4	4	4
$\rho_c$ /gcm <sup>-3</sup>	1.621	1.735	2.015
$\mu$ /mm <sup>-1</sup>	4.528	11.646	8.122
<i>F</i> (000)	936	1008	1136
$\theta$ range/°	3.88 to 67.49	3.88 to 67.50	2.40 to 25.50
completeness to $\theta_{full}$	100.0 %	100.0 %	100.0 %
reflections collected	10616	12387	7717
independent reflections	3396 [ <i>R</i> (int) = 0.0256]	3502 [ <i>R</i> (int) = 0.0332]	3654 [ <i>R</i> (int) = 0.0294]
absorption correction	analytical	analytical	analytical
max. and min. transmission	0.832, 0.702	0.760, 0.547	0.434, 0.179
data/restraints/parameters	3396 / 0 / 261	3502 / 0 / 261	3654 / 0 / 261
goodness-of-fit on <i>F</i> <sup>2</sup>	1.042	1.057	1.020
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0258, w <i>R</i> 2 = 0.0644	<i>R</i> 1 = 0.0279, w <i>R</i> 2 = 0.0706	<i>R</i> 1 = 0.0287, w <i>R</i> 2 = 0.0643
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0295, w <i>R</i> 2 = 0.0669	<i>R</i> 1 = 0.0327, w <i>R</i> 2 = 0.0736	<i>R</i> 1 = 0.0358, w <i>R</i> 2 = 0.0689
largest diff. peak and hole (eÅ <sup>-3</sup> )	0.323, -0.449	1.212, -0.592	0.959, -1.030



**Fig. S1** SEM images of xerogels of a) Cu(II):L1, c) Hg(II):L2; TEM images of xerogels of b) Cu(II):L1, d) Hg(II):L2

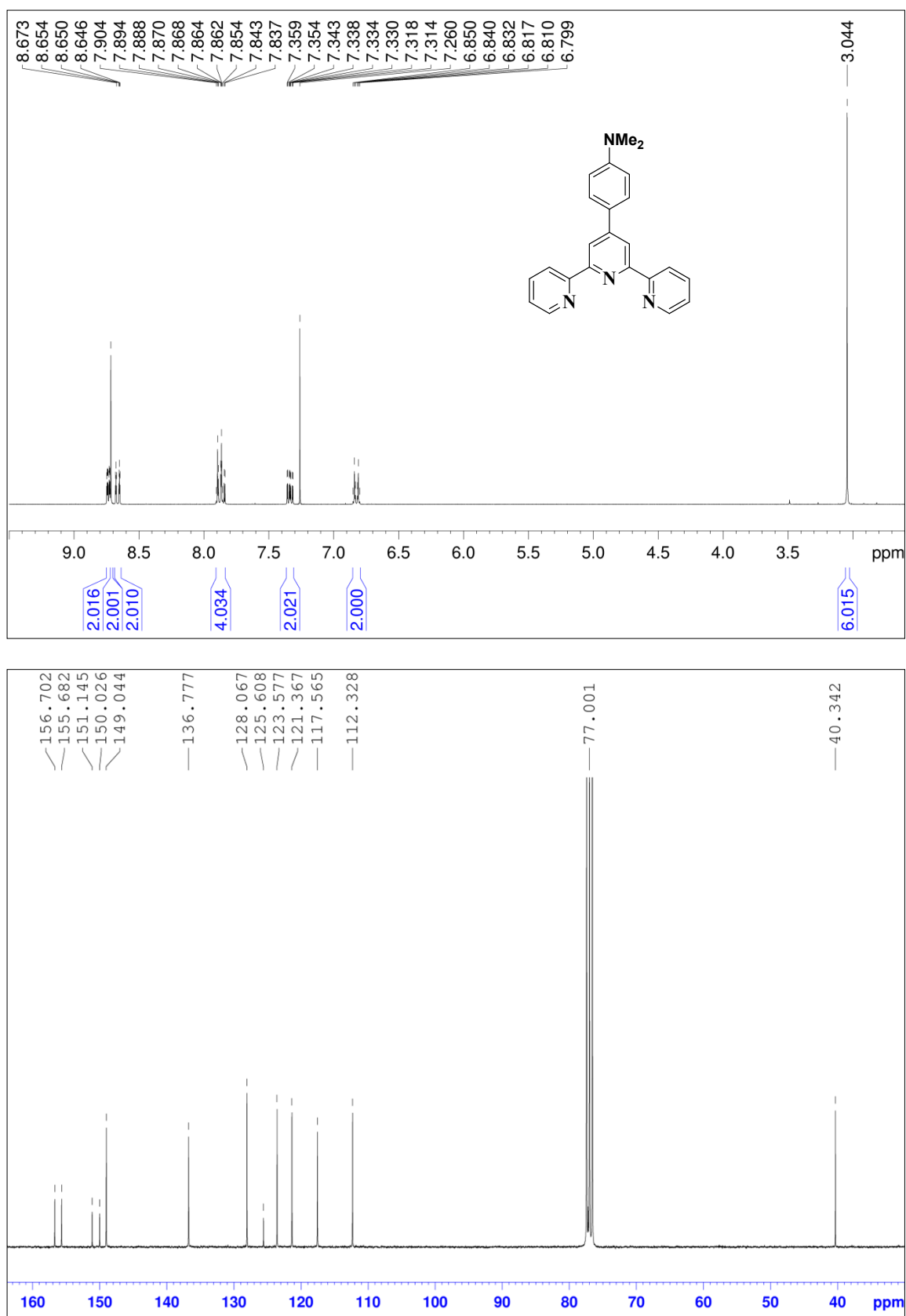
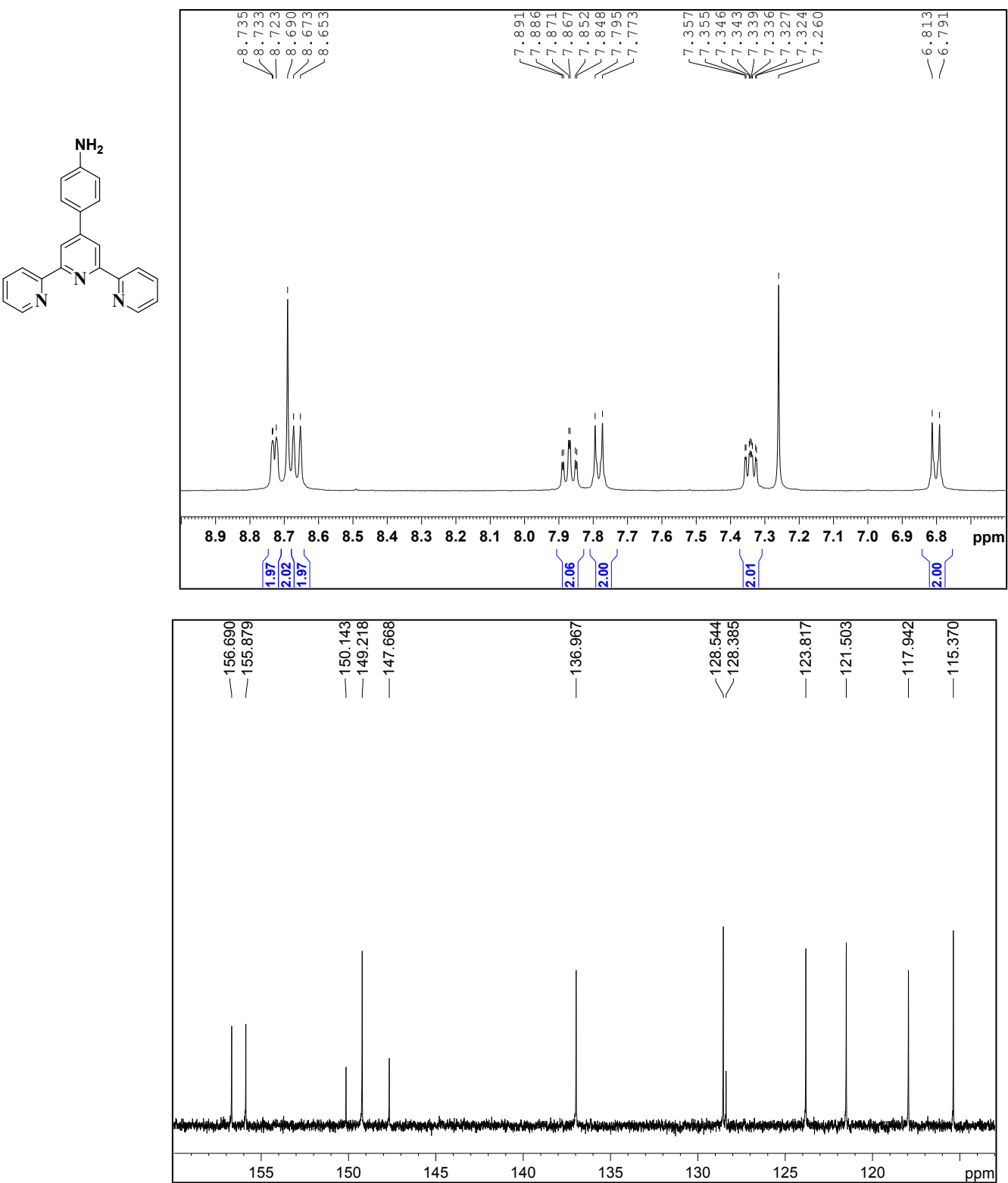
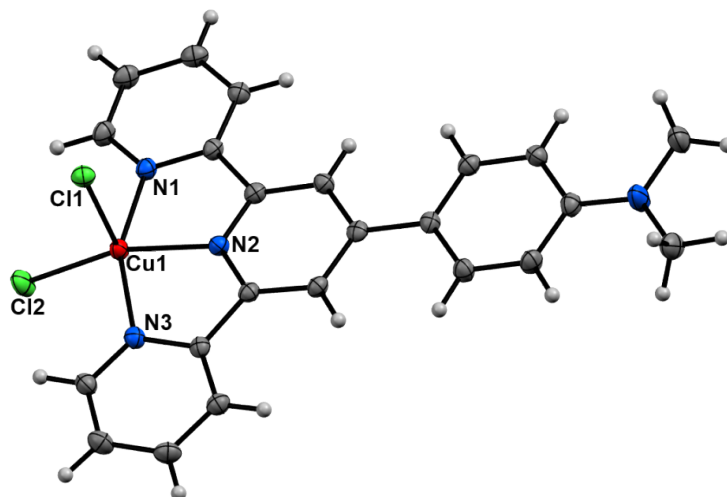


Fig. S2 <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of L1 in CDCl<sub>3</sub>.

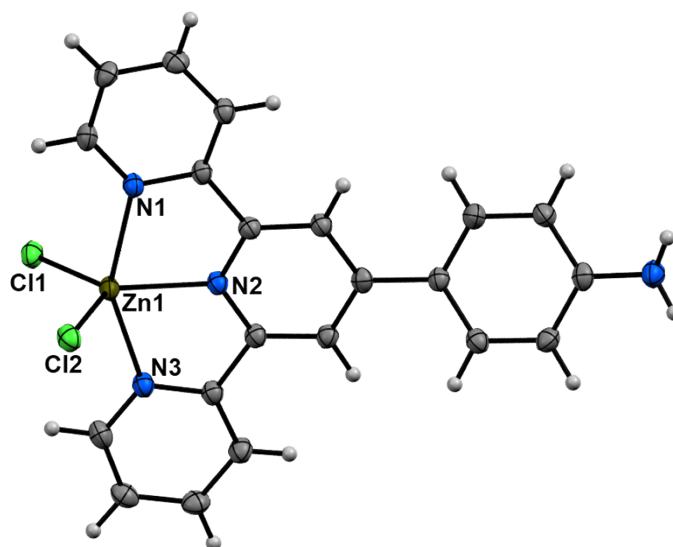




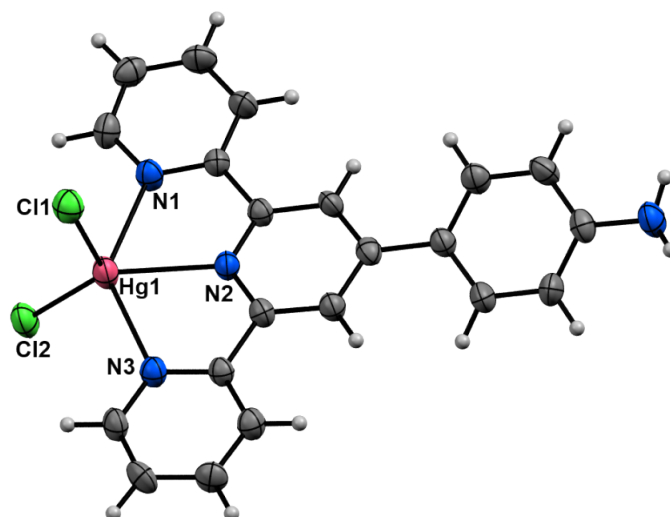
**Fig. S3** <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of L2 in CDCl<sub>3</sub>.



**Fig. S4** ORTEP plot of the molecular structure of  $\text{CuCl}_2(\text{L1})$ . Thermal ellipsoids are shown at 50% probability level. Solvated DMF molecule omitted for clarity. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Cu(1)-N(1) 2.0425(19), Cu(1)-N(2) 1.9560(19), Cu(1)-N(3) 2.0374(18), Cu(1)-Cl(1) 2.4851(6), Cu(1)-Cl(2) 2.2431(6), Cl(1)-Cu(1)-Cl(2) 107.49(2), N(2)-Cu(1)-N(1) 78.90(7), N(2)-Cu(1)-N(3) 78.75(7).



**Fig. S5** ORTEP plot of the molecular structure of  $\text{ZnCl}_2(\text{L2})$ . Thermal ellipsoids are shown at 50% probability level. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ): Zn(1)-N(1) 2.1906(16), Zn(1)-N(2) 2.0794(16), Zn(1)-N(3) 2.1809(17), Zn(1)-Cl(1) 2.2574(5), Zn(1)-Cl(2) 2.3030(5), Cl(1)-Zn(1)-Cl(2) 119.31(2), N(2)-Zn(1)-N(1) 75.47(6), N(2)-Zn(1)-N(3) 74.85(6).



**Fig. S6** ORTEP plot of the molecular structure of HgCl<sub>2</sub>(L<sub>2</sub>). Thermal ellipsoids are shown at 50% probability level. Selected bond distances (Å) and angles (°): Hg(1)-N(1) 2.415(4), Hg(1)-N(2) 2.370(3), Hg(1)-N(3) 2.410(4), Hg(1)-Cl(1) 2.4942(13), Hg(1)-Cl(2) 2.4101(13), Cl(1)-Hg(1)-Cl(2) 122.46(4), N(2)-Hg(1)-N(1) 67.89(13), N(2)-Hg(1)-N(3) 68.87(12).

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