Electronic Supplementary Material (ESI) for Chemical Communications

A Highly Selective, Hg^{2+} Triggered Hydrogelation: Modulation of Morphology by Chemical Stimuli

Biswa Nath Ghosh,[‡a] Sandip Bhowmik,[‡a] Prasenjit Mal[*b] and Kari Rissanen[*a]

[a]Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, 40014 Jyväskylä, Finland. Fax: +358 14 2602501; Tel: 358-50-5623721; E-mail: kari.t.rissanen@jyu.fi

[b]School of Chemical Sciences, National Institute of Science Education and Research (NISER) Bhubaneswar; Institute of Physics Campus, P.O. Sainik School; Bhubaneswar, Odisha751 005, India.

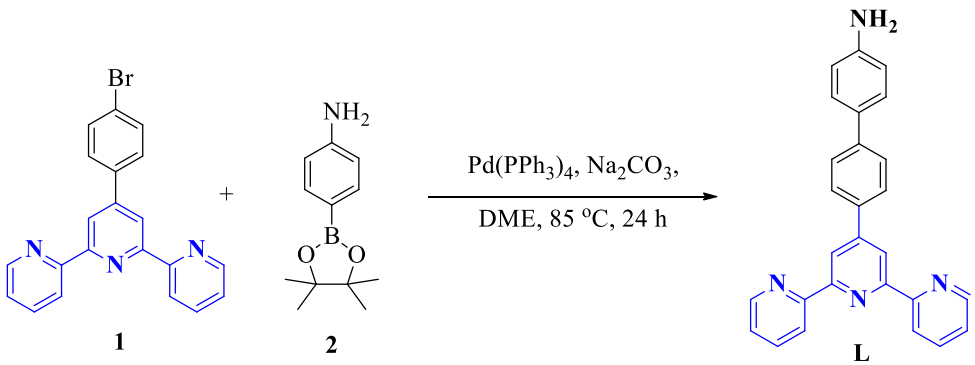
[‡]These authors contributed equally to this work.

EXPERIMENTAL SECTION

Materials and physical methods

Unless stated otherwise, all reagents and solvents were purchased from Aldrich chemicals and used without further purification. The starting compound 4′-(4-bromophenyl)-2,2′:6′,2′′-terpyridine **1** needed for the synthesis of **L** and **L1** was synthesized following the literature method.[1] The ligand 4′-[4-(4-phenyl)phenyl]- 2,2′:6′,2′′-terpyridine **L1** was synthesized according to the literature procedure.[2] The synthesis details of **L** are given below. The NMR spectra (^{1}H, ^{13}C) for **L** were recorded at 300 K on a Bruker Avance DRX500 NMR spectrometer, operating at 500 MHz for proton and 125 MHz for carbon using $CDCl_3$ as solvent. Mass spectrum was recorded on a Micromas (ESI-TOF) spectrometer.

Synthesis of 4′-[4-(4-aminophenyl)phenyl]- 2,2′:6′,2′′-terpyridine L



4′-(4-bromophenyl)-2,2′:6′,2′′-terpyridine **1** (389 mg, 1.0 mmol), 4-aminophenylboronic acid pinacol ester (241 mg, 1.1 mmol, 1.1 equiv.) and dimethoxymethane (15 mL) were placed in an oven-dried Schlenk tube and the solution was degassed and then placed under argon. Sodium carbonate (320 mg, 3 mmol) was dissolved in 6 mL water in a separate Schlenk and degassed similarly. The catalyst, $[Pd(PPh_3)_4]$, (50 mg, 0.043 mmol, 0.043 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 ^oC for 24 h. After cooling down, the solution was diluted with dichloromethane and filtered over celite. The filtrate washed with saturated NH_4Cl, brine, dried ($MgSO_4$) and evaporated to get the crude product **L**. The crude product was purified by Column chromatography (25% ethyl acetate in n-hexane) and then recrystallized from boiling ethanol solution. Yield 74%. ^1H NMR (500 MHz, $CDCl_3$) δ/ppm: 8.79 (s, 2H), 8.75 (m, 2H), 8.68 (dt, 2H, J = 1.0 Hz, 7.9 Hz), 7.97 (dt, 2H, J = 2.0 Hz, 8.5 Hz), 7.88 (m, 2H), 7.69 (dt, 2H, J = 2.0 Hz, 8.5 Hz), 7.51 (dt, 2H, J = 2.0 Hz, 8.6 Hz), 7.36 (m, 2H), 6.79 (dt, 2H, J = 2.0 Hz, 8.6 Hz), 3.78 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ/ppm: 156.58, 156.13, 150.08, 149.31, 146.39, 142.00, 136.98, 136.33, 130.83, 128.18, 127.78, 126.88, 123.92, 121.53, 118.76, 115.58. HRMS (ESI-TOF) m/z $[M+Na]^+$ calcd for ($C27H20N4Na^+$) 423,1580; found: 423,1597.

NMR characterization of L1: ^1H NMR ($CDCl_3$, 300 MHz): δ 8.81 (s, 2H), 8.75 (d, 2H, J = 3.8 Hz), 8.69 (d, 2H, J = 8.0 Hz), 8.01 (d, 2H, J = 8.3 Hz), 7.89 (td, 2H, J = 1.8, 7.8 Hz), 7.75 (d, 2H, J = 8.2 Hz), 7.68 (d, 2H, J = 7.1 Hz), 7.49 (t, 2H, J = 7.2 Hz), 7.37 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.48, 156.17, 149.93, 149.31, 142.02, 140.61, 137.48, 137.00, 129.02, 127.88, 127.76, 127.29, 123.96, 121.53, 118.87.

Gelation studies of L with MCl_2 salts (M = Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg): To a stock solution of **L** (400 µL, 8.25 mM in 0.15 N HCl) taken in a test tube (0.5 cm diameter), 120 µL of MCl_2 (55 mM in H_2O) was added from top and shaken gently to allow homogeneous mixing. Addition of Hg^{2+} produced a gel almost instantaneously whereas other divalent metal cations produced colored precipitates within 5-10 minutes (except for Zn^{2+} where precipitate was obtained after ~24 hrs). Addition of Cu^{2+} immediately produced brown gelatinous precipitate which then quickly turned to green precipitate (within 2-3 minutes).

Gelation studies with water soluble HgX_2 salts (X = NO_3, ClO_4): To a stock solution of **L** (400 µL, 8.25 mM in 0.15 N HCl) taken in a test tube (0.5 cm diameter), 120 µL of HgX_2 (55 mM in H_2O) was added and shaken gently. While $Hg(NO_3)_2$ also showed similar gelation behavior, addition of $Hg(ClO_4)_2$ to the solution of **L** resulted in a precipitate.

We also tried different mineral acids for the initial solubilization of the ligand **L**. **L** could not be solubilized in 0.2 N H_2SO_4 or $HClO_4$ even at lower concentrations (< 5 mM) and was only soluble in 0.2 N HNO_3 at elevated temperature (> 80 ^oC). However, addition of $HgCl_2$ in a hot, 0.2 N HNO_3 solution of **L** initially resulted in a clear solution that eventually turned into precipitate upon standing for long time (Fig. S1).

Gelation studies of L1 with $HgCl_2$: To a stock solution of **L1** (400 µL, 8.25 mM in 0.15 N HCl), addition of 120 µL of $HgCl_2$ (55 mM in H_2O) solution resulted precipitation of the complex (Fig. S1).

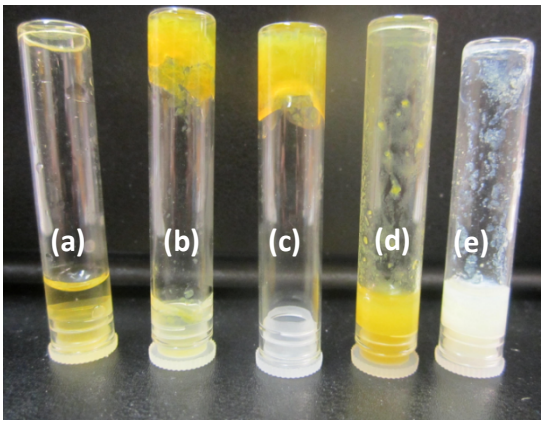


Fig. S1 6 mM of **L** in presence of (a) 12 mM $HgCl_2$ in 0.2 M HNO_3, (b) 12 mM $Hg(NO_3)_2$ in 0.2 M HCl, (c) 12 mM $HgCl_2$ in 0.2 M HCl, (d) 12 mM $Hg(ClO_4)_2$ in 0.2 M HCl and (e) 6 mM of **L1** in presence of 12 mM $HgCl_2$ in 0.2 M HCl.

Gelation study with Hg^{2+} in presence of other metal ions: To a stock solution of **L** (400 µL, 8.25 mM in 0.15 N HCl) taken in a test tube (0.5 cm diameter), a mixture of 60 µL of M^{2+} (55 mM Zn^{2+}/Cu^{2+}/Ni^{2+}) and 60 µL of Hg^{2+} (55 mM in H_2O) was added and allowed to stand after gentle shaking. It was observed while presence of Cu^{2+} and Ni^{2+} severely disturbed the gelation process, presence of Zn^{2+} resulted in a partial gel (Fig. S2).

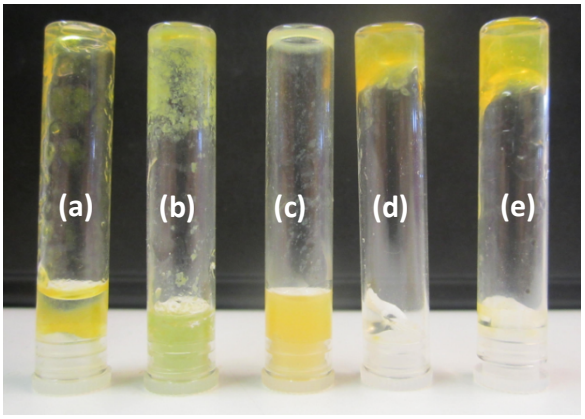


Fig. S2 6 mM of **L** in presence of 6 mM/6mM of a) Zn^{2+}/Hg^{2+}, b) Cu^{2+}/Hg^{2+}, c) Ni^{2+} /Hg^{2+}, d) 6 mM Hg^{2+} and e) 12 mM Hg^{2+}.

X-ray crystallographic details

Yellow plate like crystals of $HgCl_2$**L** were grown by slow evaporation of its DMF solution at room temperature and single crystal X-ray diffraction analysis was performed on Bruker-Nonius Kappa CCD diffractometer equipped with APEX II detector. Unit cell refinement and data reduction were carried out using the programme *DENZO-SMN*.[3] Absorption correction was done using the *SADABS*[4] programme. The structure was solved by the programme *SIR-2002*[5] and refined by full-matrix least squares on F^2 using the WinGX[6] software, which utilizes the *SHELXL-97* module.[7] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were introduced in proper positions with isotopic thermal parameters using the ´riding model´. The figures were drawn using *Ortep-3 for Windows*[8] and *Mercury* v 2.3 programmes.[9]

Table S1. Crystallographic data and structure refinement parameters for **$HgCl_2L$**

CCDC No.	960506
Empirical formula	$C_{27}H_{20}N_4Cl_2Hg_1$
Formula weight	671.96
Temperature	123.0(1) K
Wavelength	0.71073 Å
Crystal color and shape	yellow, plate
Crystal size	0.52 x 0.18 x 0.02 mm^3
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 9.2217(10) Å b = 10.8168(12) Å c = 13.0876(17) Å α = 75.035(5)° β = 69.904(6)° γ = 83.819(7)°
V	1184.2(2) $Å^3$
Z	2
Density (calculated)	1.885 Mg/m^3
Absorption coefficient	6.749 mm^{-1}
F(000)	648
Theta range for data collection	2.41 to 24.99°
Index ranges	$-10 \le h \le 10$; $-12 \le k \le 12$; $-15 \le l \le 14$
Completeness to theta = 25.00°	97.7 %
Reflections collected	6906
Independent reflections	4069 [R(int) = 0.0404]
Absorption correction	multi-scan
Max. and min. transmission	0.7458 and 0.4592
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4069 / 0 / 308
Goodness-of-fit on F^2	1.037
Final R indices [I>2σ(I)]	R1 = 0.0452, wR2 = 0.0918
R indices (all data)	R1 = 0.0690, wR2 = 0.1022
Largest diff. peak and hole	0.823 and -0.668 $e.Å^{-3}$

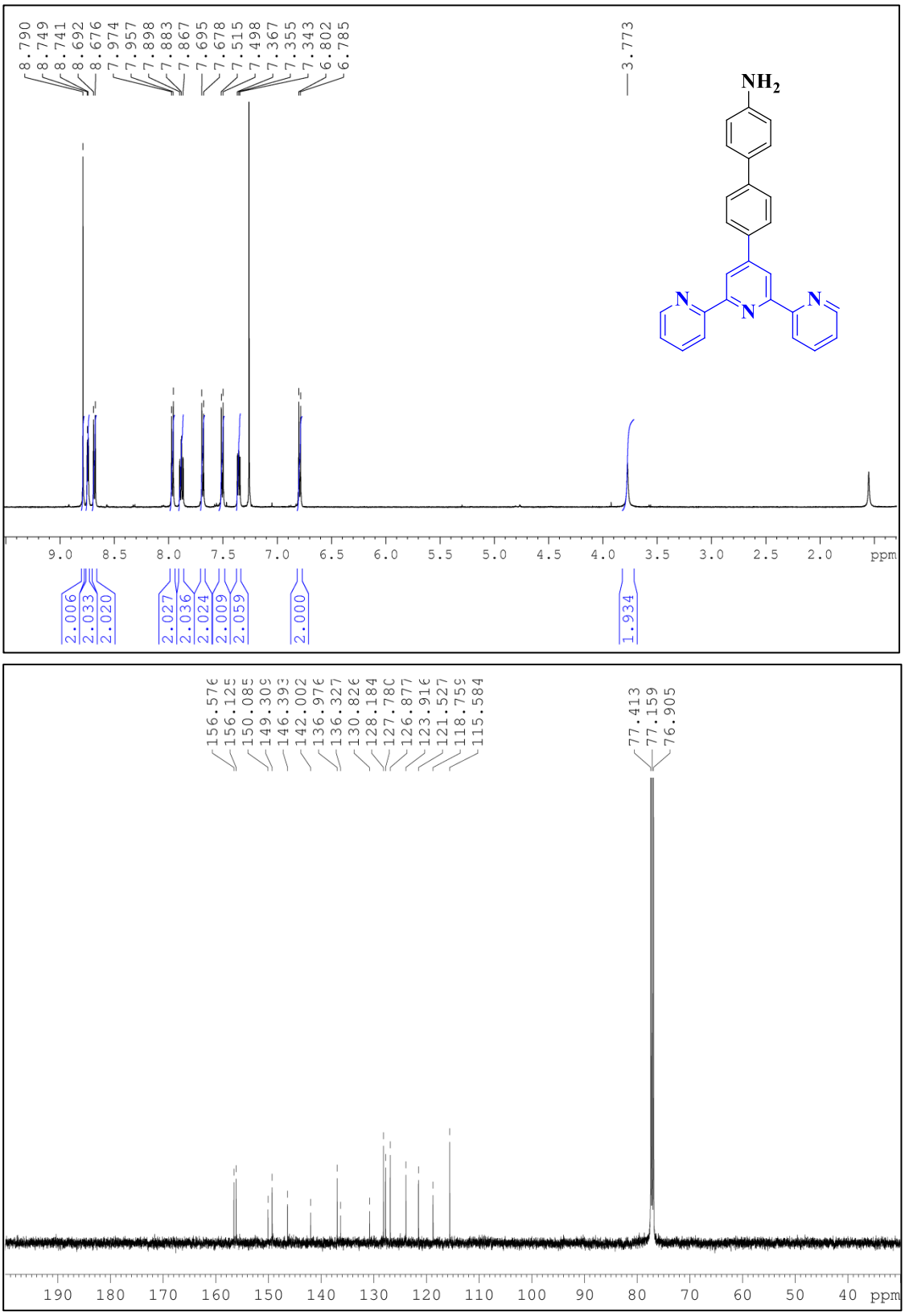


Fig. S3 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **L** in $CDCl_3$.

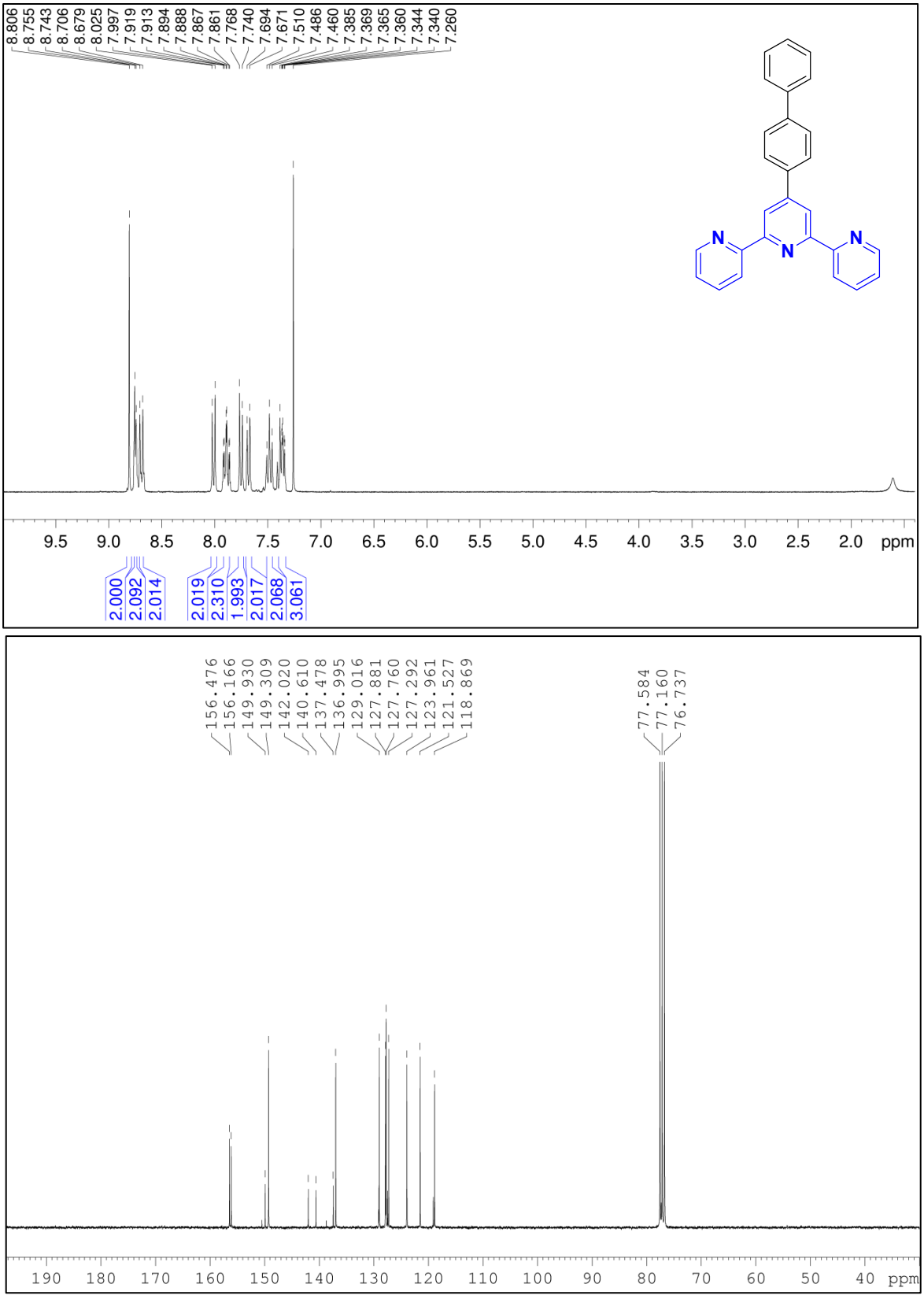


Fig. S4 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **L1** in $CDCl_3$.

References

1. F. S. Han, M. Higuchi and D. G. Kurth, *Org. Lett.*, 2007, **9**, 559-562.
2. W. Goodall, K. Wild, K. J. Arm and J. A. G. Williams, *J. Chem. Soc.*, *Perkin Trans. 2*, 2002, 1669-1681.
3. Z. Otwinowski and W. Minor, *Methods in Enzymology*, *Macromolecular Crystallography*, *Part A*, New York: Academic Press, 1997.
4. G. M. Sheldrick, *SADABS, Bruker Analytical X-ray system, Inc., Madison, Wisconsin*, 2008.
5. M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 2005, **38**, 381-388.
6. L. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837-838.
7. G. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.
8. L. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849-854.
9. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466-470.