Electronic Supplementary Material (ESI) for Analyst

Intermolecular approach to metal ion indicators based on polymer phase transitions coupled to fluorescence resonance energy transfer

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Thermal Quenching Experiment

The ratiometric measurement won't be interfered by thermo quench because both donor and acceptor were quenched at the same extent. This can be observed in Fig. 5 (B), the ratio of acceptor to donor remain unchanged although temperature is being increased from 20 °C to 32 °C before phase transition (0-24 min). Therefore thermo quench won't affect the FRET. Figure 6 depicts the fluorescence intensities of both donor and acceptor lost a small fraction of total fluorescence, only 10%, although Cu(II) were in presence at high concentration of 1×10^{-4} M. However, ratio of donor to acceptor emission intensity remains unchanged with different Cu(II) concentrations; therefore ratiometry circumvents the problem of copper quenching.

The environment surrounding dyes changes between hydrophilic and hydrophobic as the thermal phase transition takes place. Changes in environment also led to fluctuations of fluorescence; however, the fluorescence fluctuations are canceled out by ratiometry since environmental impacts on them are at the same extent.

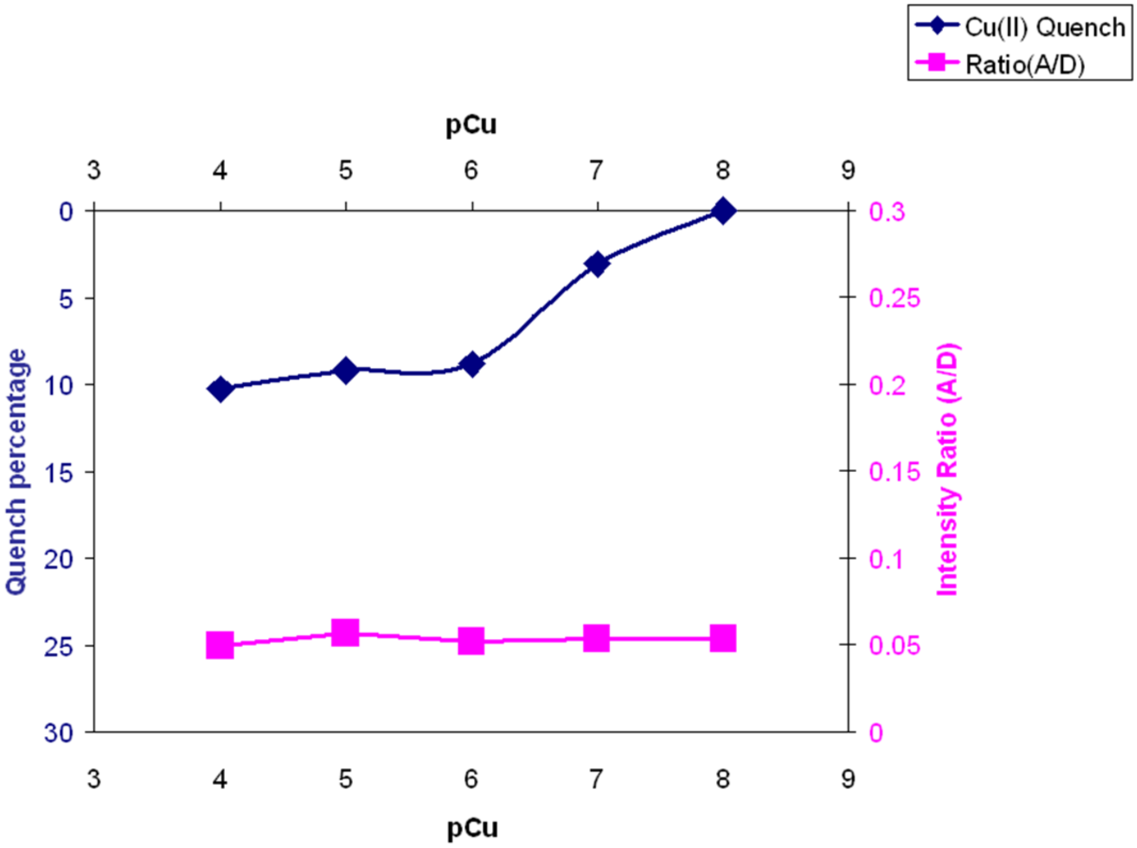


Figure S1. Thermal quenching and Cu(II) quenching effects on ratometric fluorescence. Left axis (Y1) represents absolute fluorescence intensity quenched by Cu(II). Right axis (Y2) represents the ratiometric response to Cu(II).

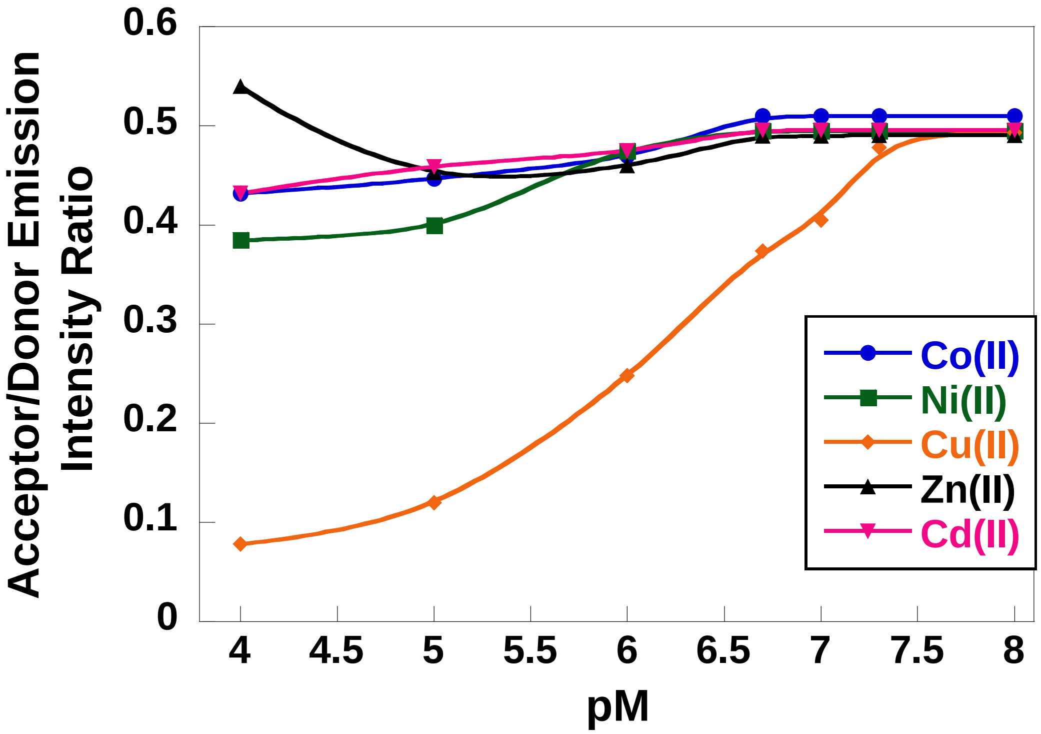


Figure S2. Changes in the acceptor/donor emission intensity ratio upon the addition of various metal ions.

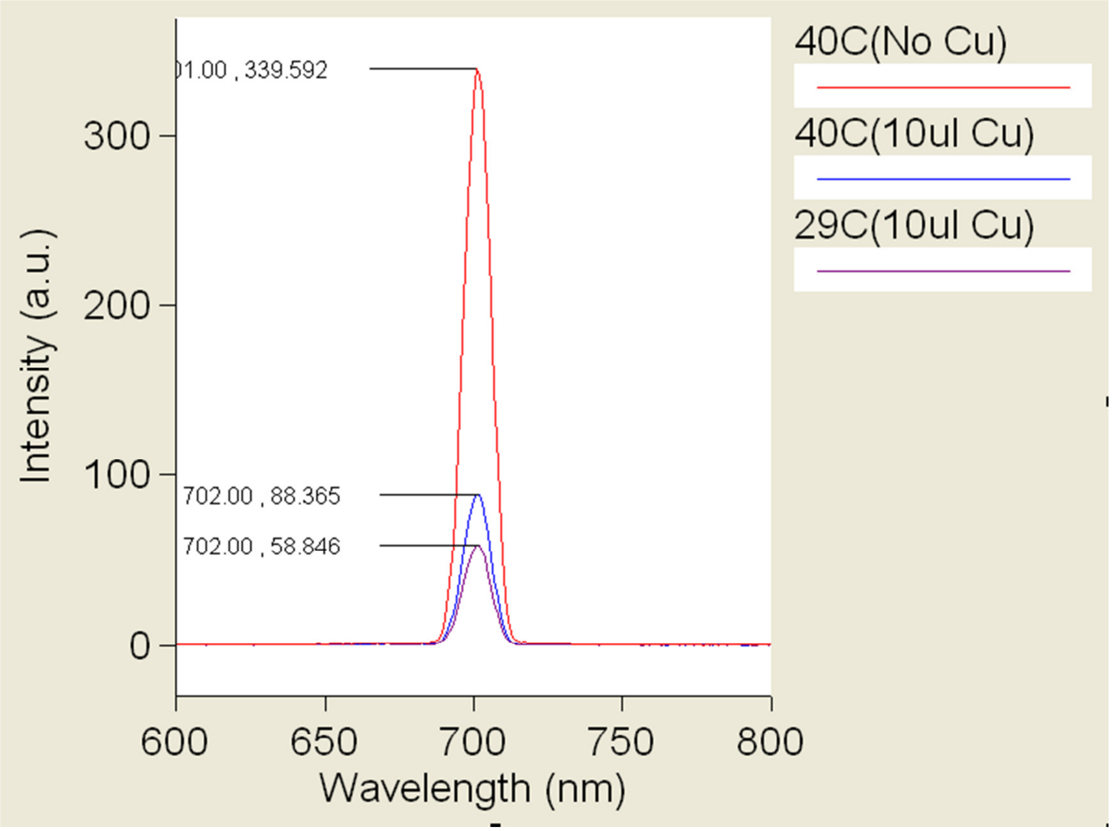
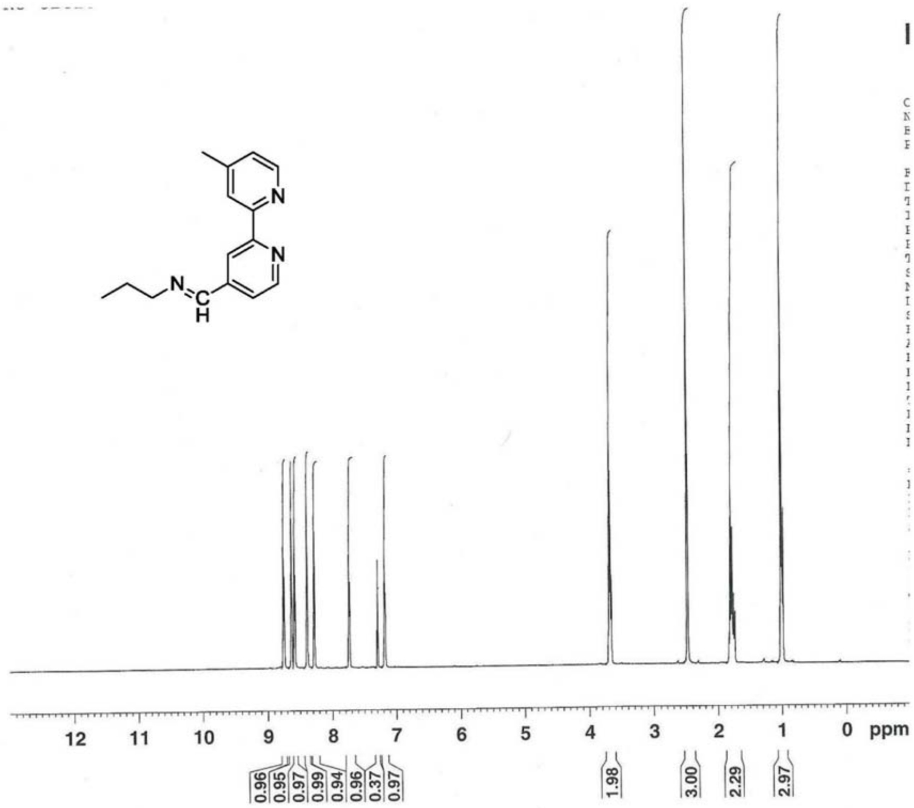
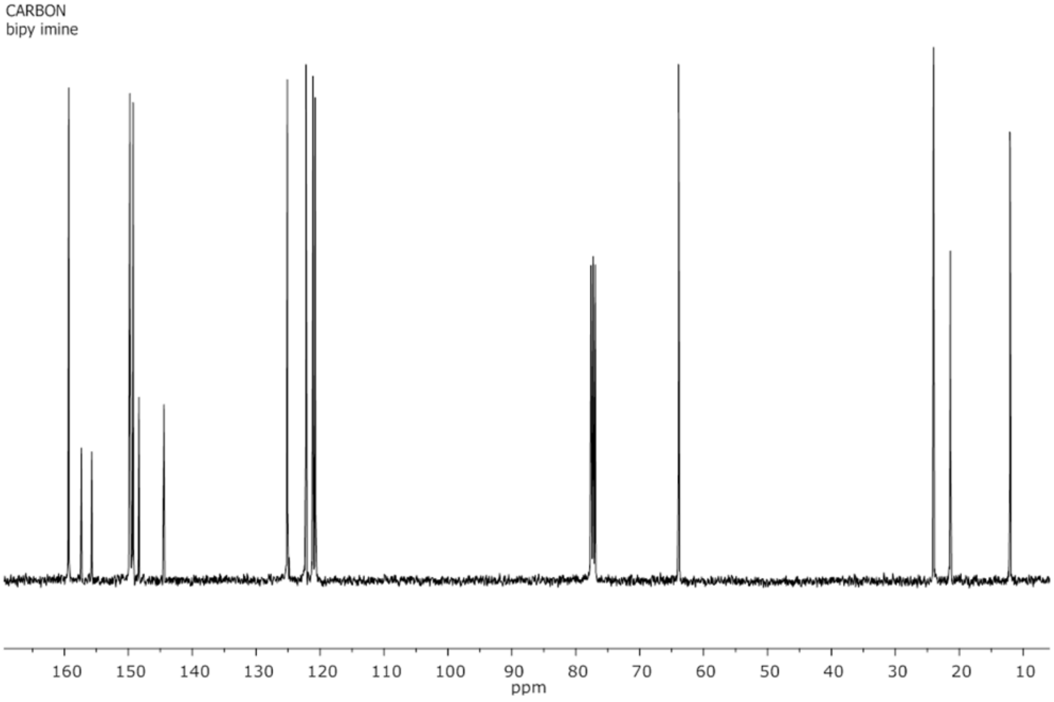
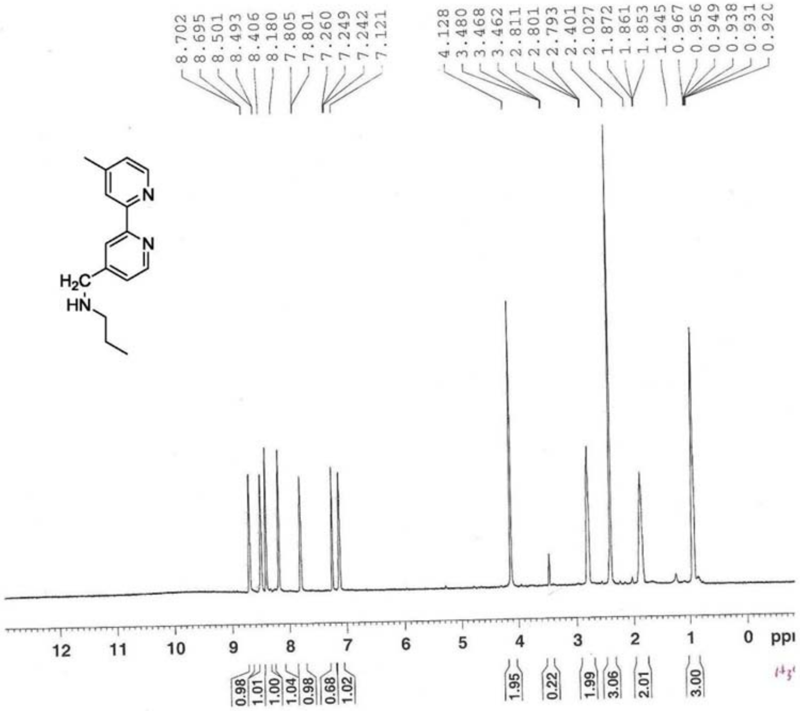


Figure S3. Second order scattering (SOS) intensities in dynamic light scattering. Measurements were performed with 1 × 10^{-5} M indicator in water. At 40 °C (red curve), the intense peak from scattering indicates the presence of aggregated polymer. Upon the addition of 10µ L Cu(II) stock solution to give a final [Cu(II)] of 1 × 10^{-4} M (blue curve), the particles disaggregate as indicated by the decreased scattering. Subsequent decrease of the temperature to 29 °C (purple curve) shows very little evidence of further disaggregation, which suggests that the Cu(II) efficiently causes the particles to disaggregate. Settings: exciting wavelength, 350 nm, emission wavelength, 700 nm.

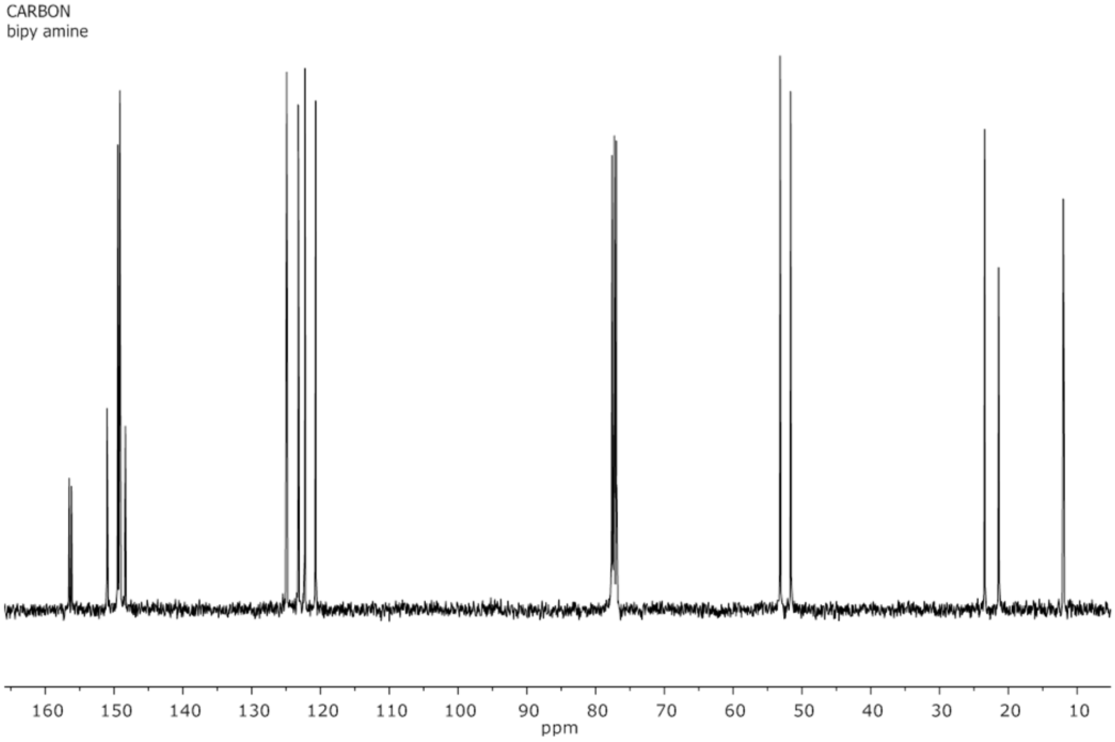


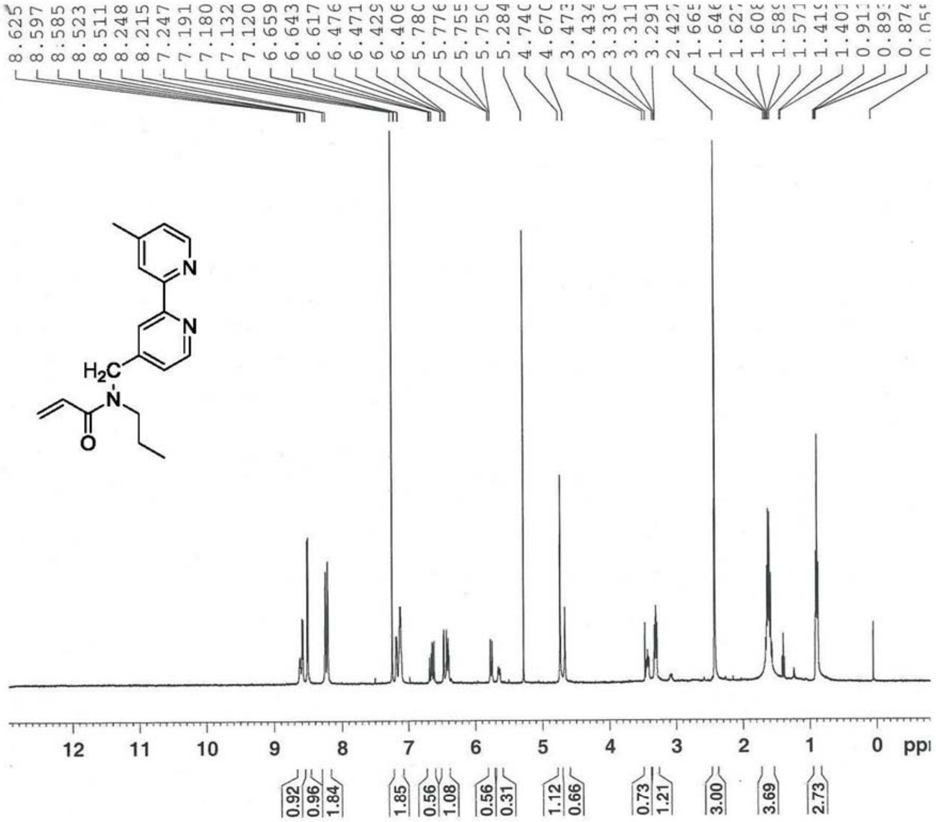
^{13}C NMR (101 MHz, CDCl$_3$) δ 159.33, 157.35, 155.71, 149.76, 149.24, 148.36, 144.44, 125.11, 122.19, 121.10, 120.75, 63.89, 24.04, 21.40, 12.05.



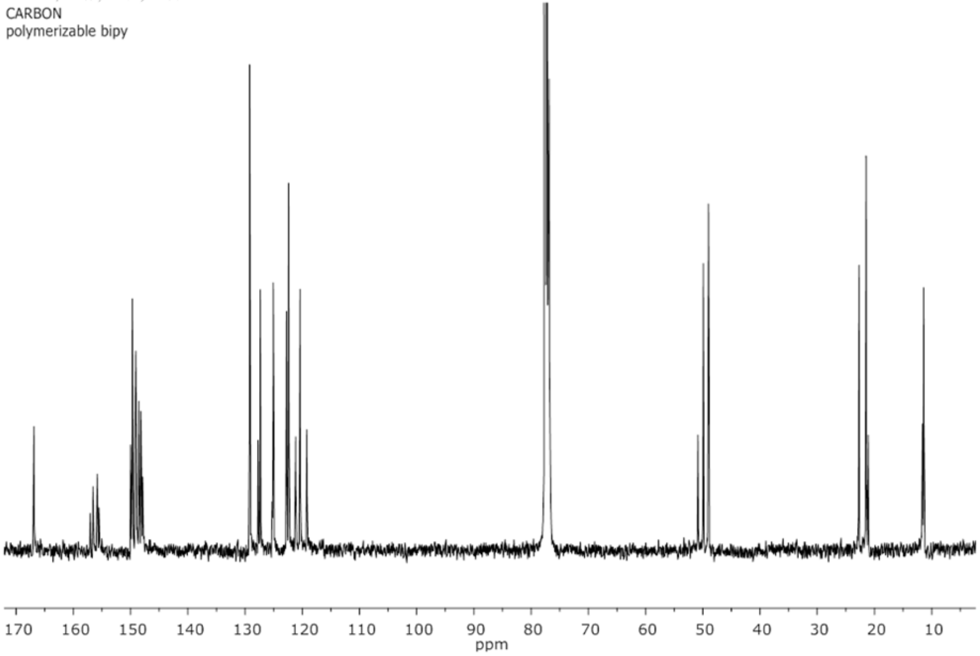


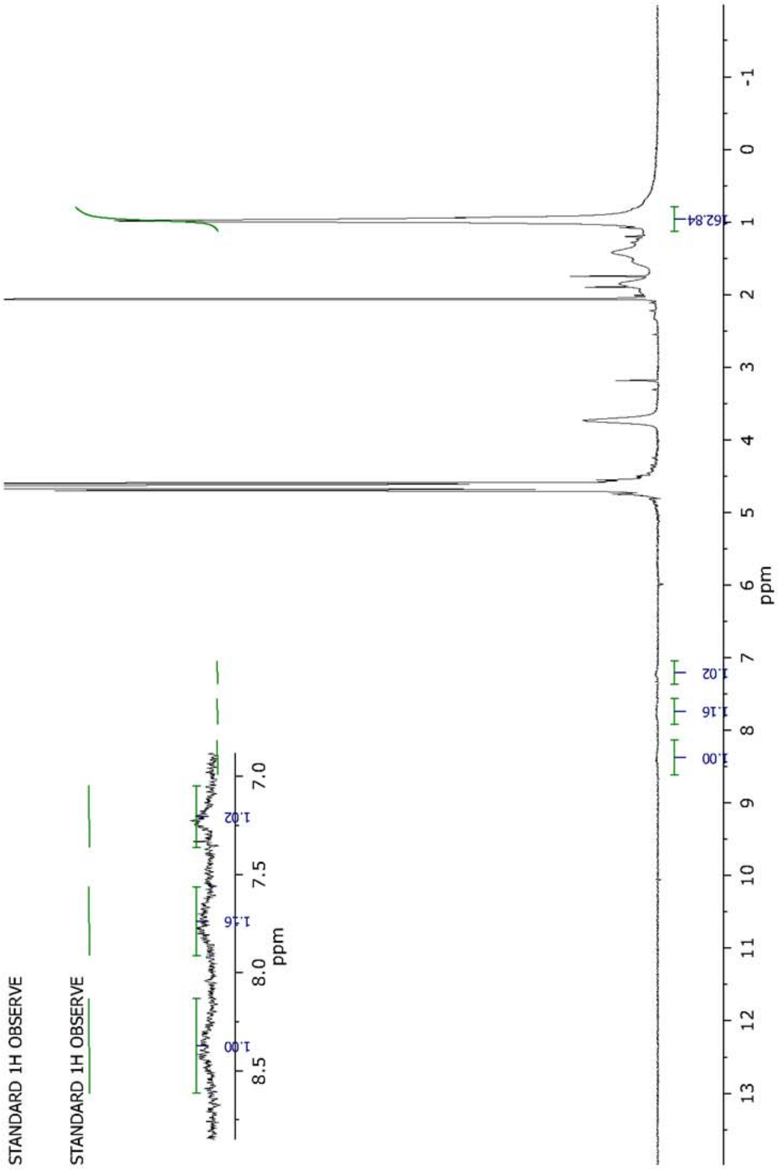
^{13}C NMR (101 MHz, CDCl$_3$) δ 156.49, 156.16, 150.99, 149.41, 149.15, 148.33, 124.89, 123.19, 122.22, 120.67, 53.15, 51.62, 23.43, 21.39, 11.97.





^{13}C NMR (101 MHz, CDCl$_3$) δ 167.01, 166.91, 157.03, 156.57, 155.83, 155.53, 149.98, 149.68, 149.22, 149.08, 148.55, 148.20, 147.90, 129.18, 127.72, 127.32, 125.24, 125.06, 122.74, 122.36, 121.16, 120.39, 119.19, 50.84, 49.91, 48.99, 22.71, 21.44, 21.09, 11.62, 11.37.





NMR of indicator. The ratio of propyl hydrogen atoms ~1 ppm to the pyridyl hydrogen atoms 7-8.5 ppm allows the % of ligand to be calculated.