

Supporting information

Chromo-luminescent selective detection of fluoride ion by Copper(II) bis(terpyridine) complex solution via displacement approach

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Synthesis of 4'-(4-N,N'-dimethylaminophenyl)-2,2':6',2''-terpyridine Ligand (L)

2-Acetylpyridine (4.5 mL, 40 mmol) was added to a solution of 4-dimethyl amino benzaldehyde (3.0 g, 20 mmol) in EtOH (60 mL). Potassium hydroxide (KOH) pellets (3.4 g, 51 mmol) and aq. NH₃ (58 mL, 25%, 6.3 mmol) was then added to the solution. The solution was stirred at Room temperature for 30 h. The precipitate was filtered and subsequently washed several times with ethanol, water, and diethyl ether. The product thus obtained was re-dissolved in a minimal volume of chloroform and nearly 3.5 times (excess) of n-hexane was added to get precipitate. Then the resulting precipitate was filtered and washed with a mixture of chloroform and n-hexane (1:3.5 v/v) and was dried under vacuum to get yellow powder of the ligand **L**. Yield = 31%.

¹H NMR (400MHz, CDCl₃) δ/ppm: 8.74-8.72 (d, 2H), 8.71 (s, 2H), 8.67 (d, 2H), 7.89-7.84 (m, 4H), 7.35-7.32 (m, 2H), 6.83-6.80 (dt, 2H), 3.03 (s, 6H). (**Fig. S2**)

LRMS (ESI-TOF) : m/z calculated for [M+1]⁺ (C₂₃H₂₀N₄)⁺: 352.168; found: 353.142. (**Fig. S3**)

FTIR (ν) cm⁻¹ = ν(C=C)_{py} = 1592, 1579, ν(C=N)_{py} = 1461, ν(C-H)_{py} = 1121, 1070, ν(C-H)_{py} = 989, 946, 893, 817, 790, 738, 660, 621, 559 (**Fig. S6**)

Synthesis of Cu^{II} bis(terpyridine) complex

A solution of ligand **L** (0.029 g, 0.0000826 mol) in 10 mL dichloromethane was added to a solution of Copper nitrate (0.01 g, 0.0000413 mol) present in 10 mL acetonitrile and then resulting solution stirred at RT for 4 hours to get a yellowish orange precipitate. The resultant precipitate was filtered and subsequently washed with water, methanol followed by diethyl ether and dried under vacuum to get the **L**₂-Cu(II) complex. Yield = 68%.

LRMS: m/z calculated for [M+Na]⁺ (C₄₆H₄₀CuN₁₀NaO₆)⁺: 914.2326; found: 914.2297 and [M+2Na] (C₄₆H₄₀CuN₁₀Na₂O₆)⁺: 937.2223; found: 937.0987. (**Fig. S4**)

FTIR (ν) cm⁻¹ = ν(C=C)_{py} = 1588, 1539, ν_{as}(NO₂)=1475, ν(C=N)_{py} = 1444, ν_s(NO₂)=1337, ν_s(N-O) = 1018, ν(C-H)_{py} = 819, 702, 730, 689, 656, 562. (**Fig. S6**)

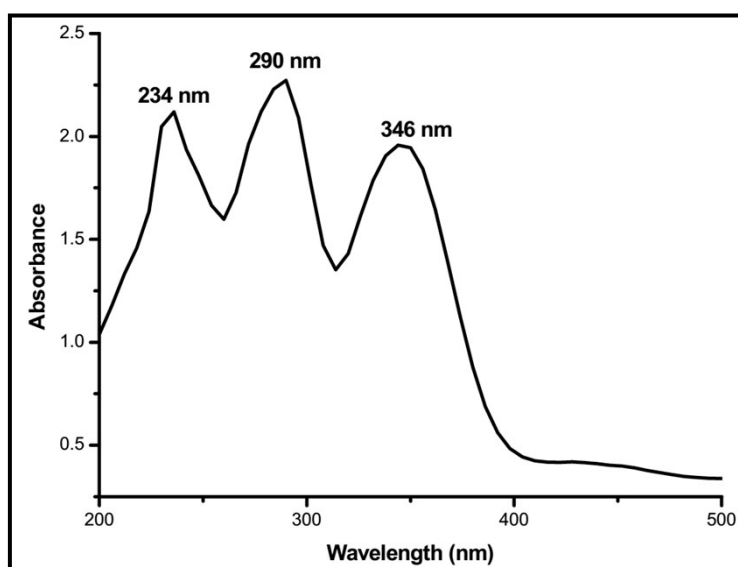


Fig. S1. UV-visible spectra of terpyridine Ligand (**L**) (10⁻⁵ M in acetonitrile).

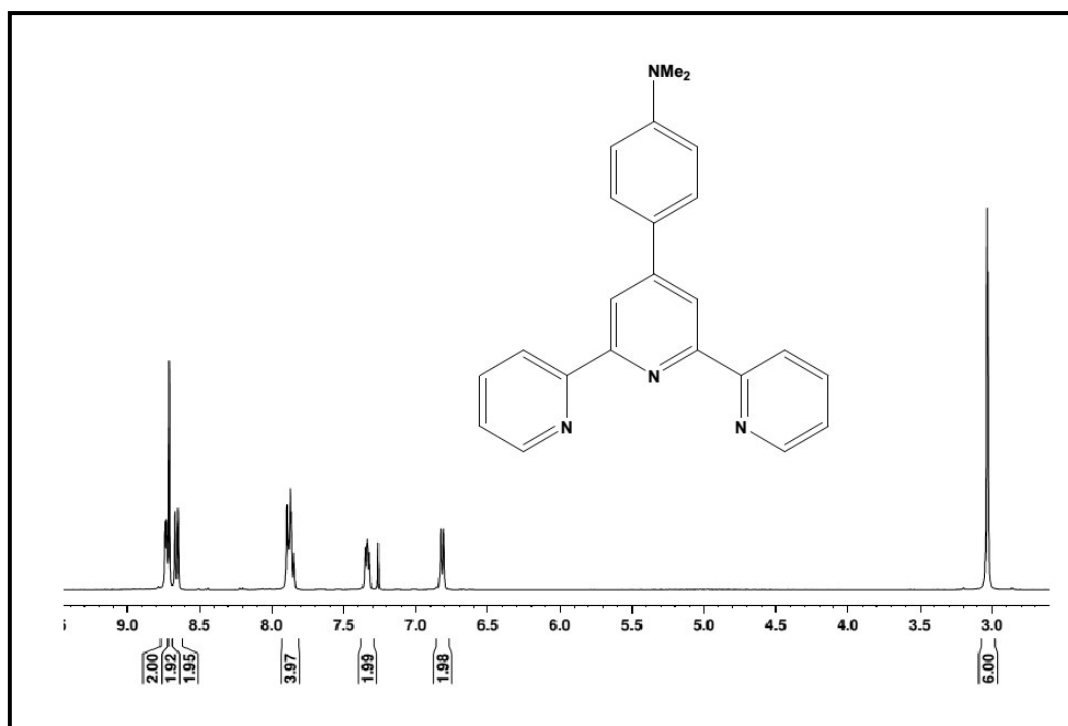


Fig. S2. ¹H NMR spectra of terpyridine Ligand (L) in CDCl₃.

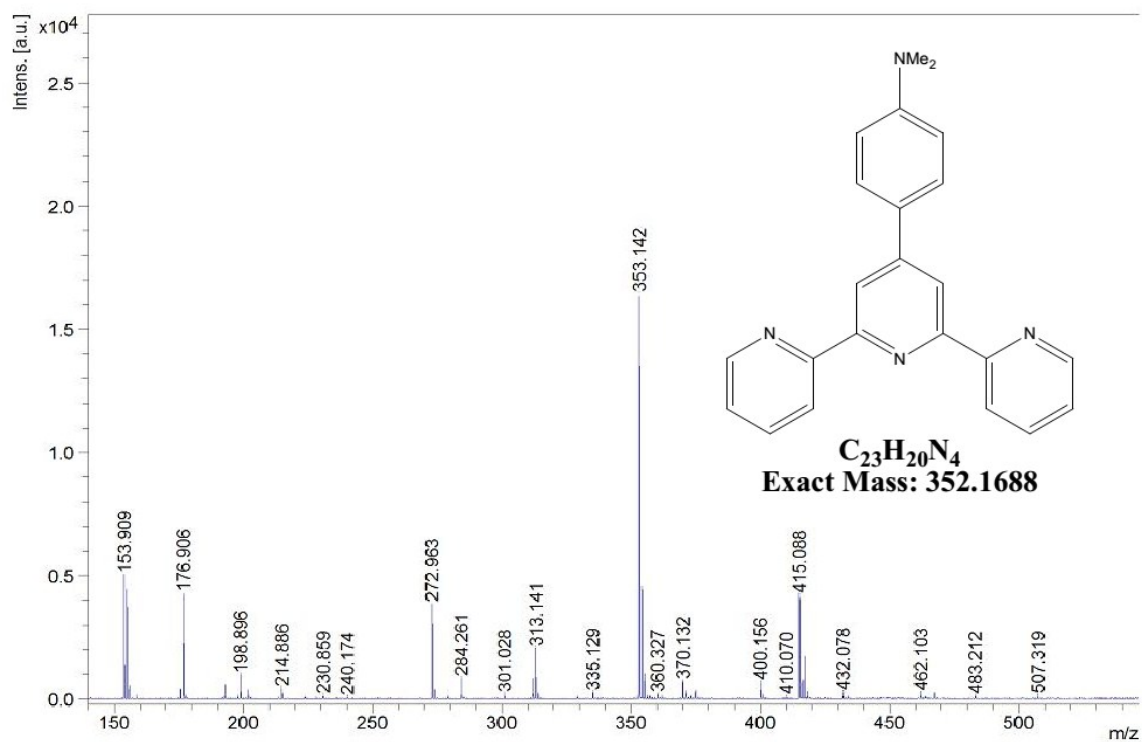


Fig. S3. Mass data for terpyridine Ligand (L).

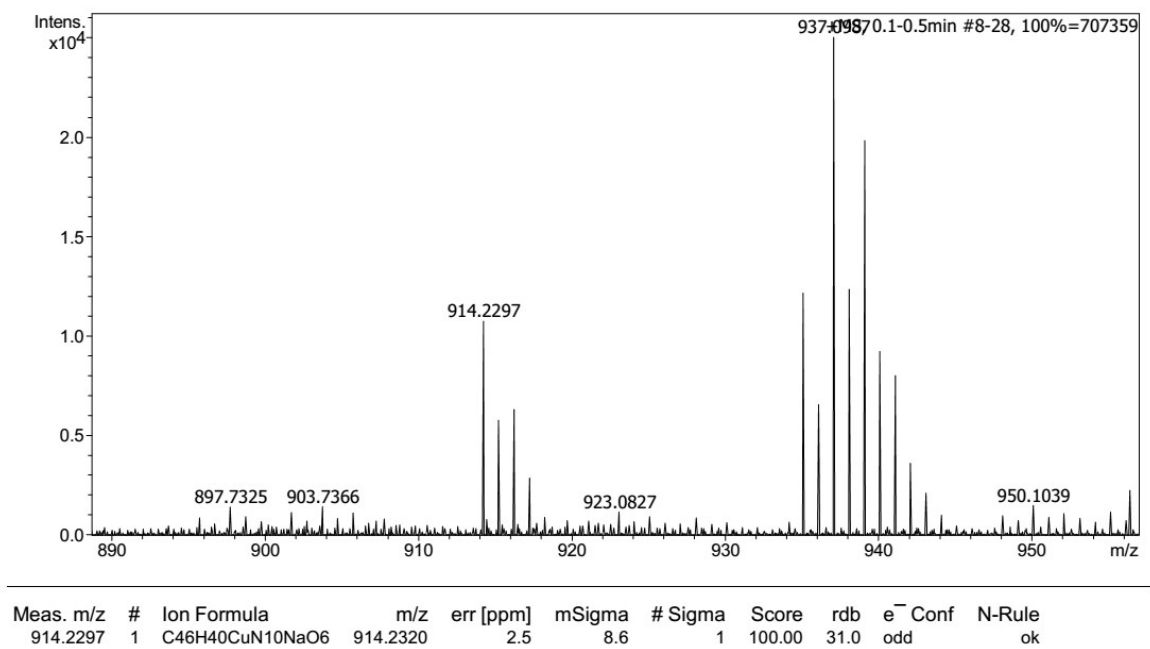


Fig. S4. LRMS spectra for Cu^{II} bis(terpyridine) complex.

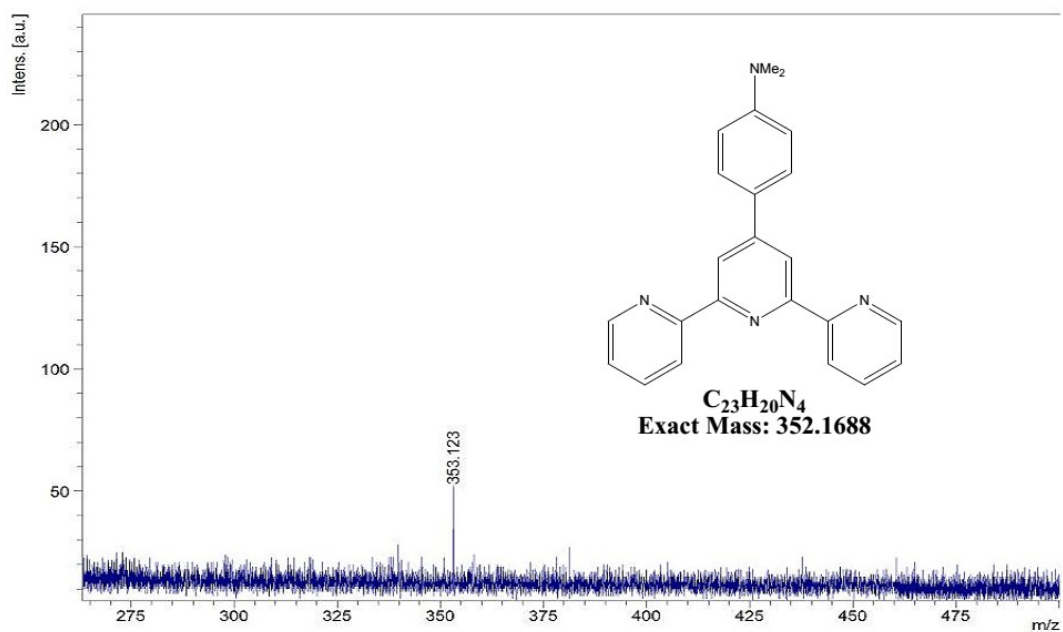


Fig. S5. Mass data for Cu(II) bis-terpyridine complex with 20 equivalents fluoride ion.

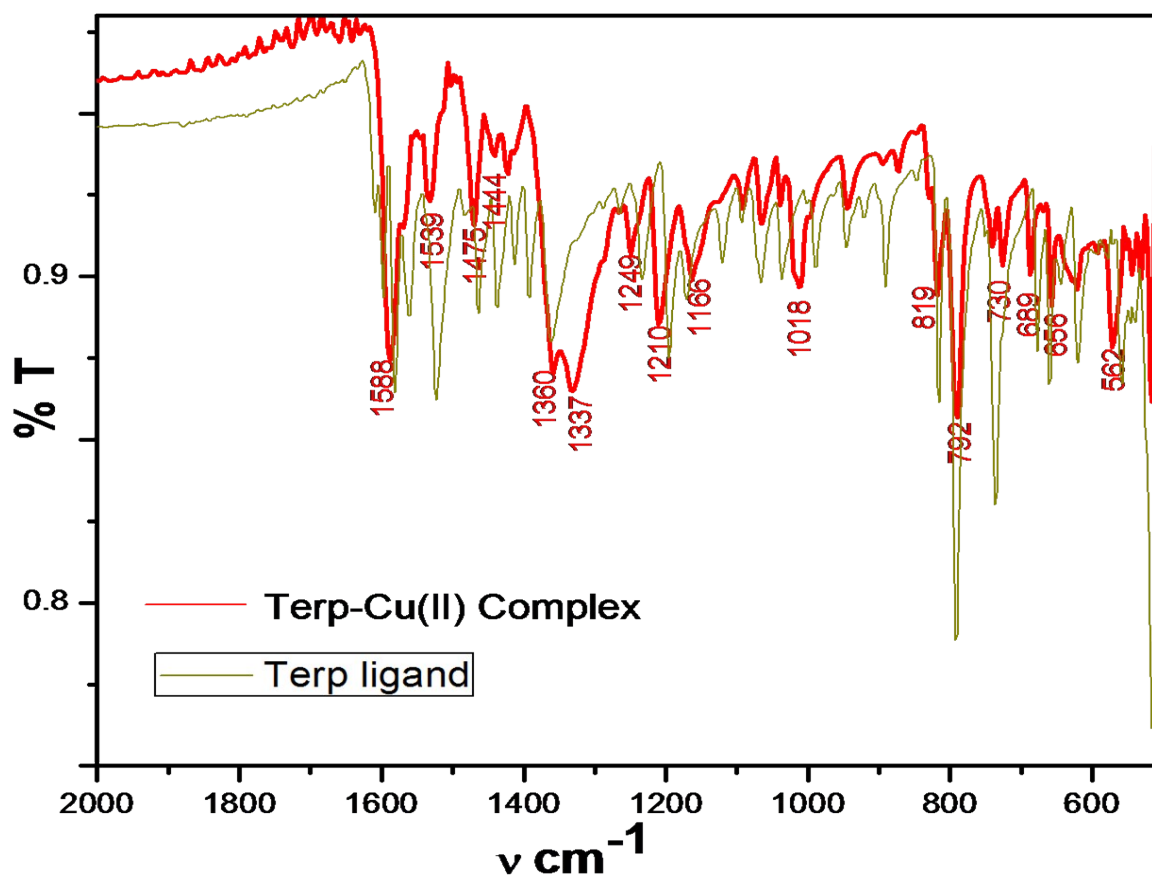


Fig. S6. FTIR of Terp-Cu(II) complex (Red line, labeled) and Terp Ligand (Gray).

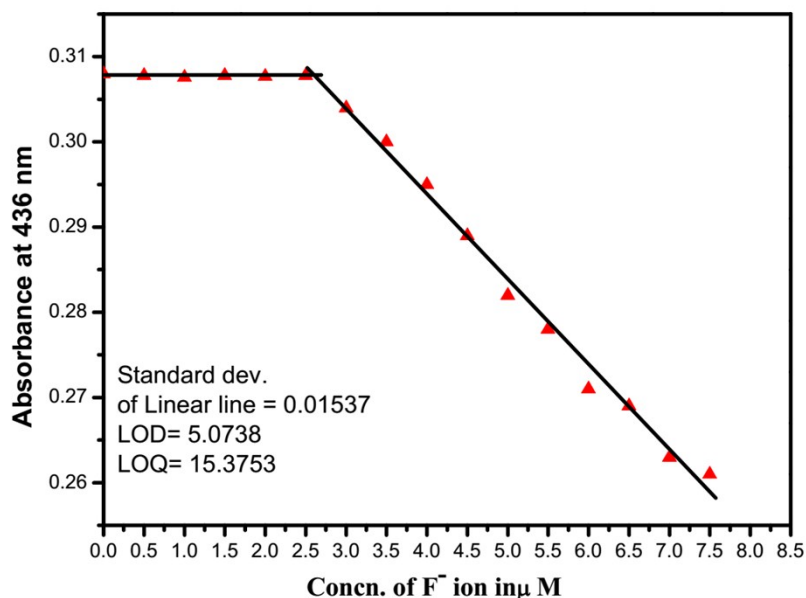


Fig. S7. Determination of limit of detection (LOD) and limit of quantification (LOQ) as a function of absorbance at 436 nm by the addition of F^- ion from a 0.1 mM stock solution of F^- ion to 2 mL of (10^{-5} M) complex solution so that the final concentration of F^- ion remain within the range of 0.5 to 8 μM .