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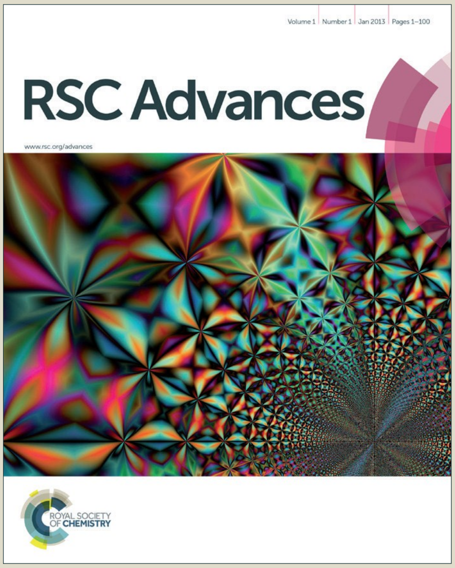

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# Synthesis and Characterization of Monometallic Rhenium(I) Complexes and their Application as Selective Sensor for Copper(II) ion

Arumugam Ramdass,[a] Veerasamy Sathish,[a] Murugesan Velayudham,[b] Pounraj Thanasekaran,*[c] Siva Umapathy,*[b] and Seenivasan Rajagopal*[a]

Novel imine functionalized monometallic rhenium(I) polypyridine complexes (**1-4**) comprising two phenol moieties attached to 2,2′-bipyridine ligands **L1**-**L4** have been synthesized and characterized. These complexes exhibit selective and sensitive detection towards copper (II) ion and this is observed through changes in UV-visible absorption, luminescence and time-resolved spectroscopic techniques. An enormous enhancement is observed in emission intensity, quantum yield and luminescence lifetime with the addition of copper(II) ion, and this can be attributed to the restriction of C=N isomerization in the Re(I) complexes. The strong binding between copper(II) ion and these complexes reveals that the binding constant values are in the range of $1.1\times10^3 – 6.0\times10^3$ $M^{-1}$. The absorption spectral behavior of the complexes is supported by DFT calculations.

## Introduction

In the recent years increasing attention has been paid to the design and fabrication of metal ion based luminescent chemo/biosensors because of their high selectivity, sensitivity, simplicity, low background noise and wide dynamic ranges.[1] Manipulating the mechanism of fluorescent probes towards the chemosensor is a challenging task and it depends on their interaction with a chemical species to produce a detectable fluorescent signal.[2] Indeed a plausible mechanism has been proposed for the sensing of chemical species through photoinduced electron/energy transfer (PET),[3] metal-to-ligand charge transfer (MLCT),[4] intramolecular charge transfer (ICT),[5] excimer/exciplex formation,[6] excited-state intra-/intermolecular proton transfer (ESIPT)[7] and C=N isomerization.[8] Of these, signalling due to C=N isomerization has occupied a prominent place in recent years, because the imine group containing fluorescent moiety is an attractive tool for optical sensing of metal ions.[9] Recently, a number of Schiff base receptors have been exploited for the fluorescent recognition of various metal ions.[10] The imine linkage in Schiff-base compounds undergoes vibrational relaxation from the excited states through fast non-radiative decay process due to C=N isomerization and hence, they are usually non-fluorescent. Hence with the addition of metal ions, it may be possible to hinder the C=N isomerization process, thereby emission intensity can be enhanced. This strategy has been followed in designing a number of C=N isomerization-based probes for sensing various metal cations.[11] Liu *et al.* reported a fluorescent Schiff-base derivative, which shows a fluorescence enhancement upon binding to $Fe^{3+}$ in aqueous solution due to the inhibition of C=N isomerization.[12]

Recently, fabrication of fluorescent chemosensors for copper ion has received a wide attention due to its significant contribution to biological, environmental, and chemical fields.[13] Rhenium(I)-tricarbonyl complexes offer a variety of applications in diverse fields *viz.* sensors,[14] catalysis,[15] light-emitting devices,[16] $CO_2$ fixation,[17] optical switches,[18] bioprobes[19] and imaging[20] as a result of rich photophysical and photochemical behavior. The coordination of Re(I) center with Schiff-base containing bipyridine ligand results in appearance of absorption band due to metal-to-ligand charge transfer (MLCT) transition in visible region, which can be utilized as a handle for optical sensing of metal ions. There is only a few reports available on rhenium(I) complexes attached to the imine ligands.[21] Pope and co-workers[14c] developed ditopic ligands, based on *N,N*-functionalized 4-aminomethylpyridine, containing rhenium(I) complexes, which have been used for sensing of metal dications of physiological and toxicological importance (Cu(II), Zn(II) and Hg(II)) by monitoring the changes in emission intensity and lifetime. Recently, we reported the application of rhenium(I) monometallic complex attached with imine ligands as optical sensor for anions.[22] Herein, we report the synthesis and characterization of four new tricarbonyl rhenium(I) complexes and their application towards the selective and sensitive sensing of copper ions through the UV–visible absorption, luminescence and time-resolved luminescence spectroscopic techniques. Furthermore, the geometry of the complexes was optimized by density functional theory (DFT) calculations and their UV-Vis absorption characteristics were supported by time dependent density functional theory (TDDFT) calculations.

## Experimental Section

### Materials

Starting materials such as $Re_2(CO)_{10}$, 4-picoline, selenium dioxide were purchased from Sigma Aldrich and used as such. Amines such as 2-aminophenol, 2-amino-4-methylphenol, 2-amino-4-tert-butylphenol and 2-amino-4-chlorophenol were purchased from Alfa Aesar. Commercial grade solvents, acetone, isooctane, ethanol and diethyl ether were used as received without further purification. Spectroscopic grade solvents including $CH_3CN$ and DMSO were used in all absorption and emission measurements. $Re(CO)_5Br$ was obtained by the oxidative addition of $Br_2$ to $Re_2(CO_{10})$.[23] 2,2′-Bipyridine-4,4′-dicarbaldehyde was synthesized by using previous literature procedure.[24]

### Instrumentation

Infrared spectra were recorded on 8400S Shimadzu-FT-IR spectrophotometer. $^1$H NMR spectra were recorded on a Bruker 300 MHz spectrometer. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents. Electrospray ionisation mass spectrometry (ESI-MS) analysis was performed on a liquid chromatography-ion trap mass spectrometer (LCQ Fleet, Thermo Fisher Instruments Limited, USA). Elemental analyses were performed using Thermo Finnigan Flash EA 1112 CHNS analyser. Raman spectra were recorded using Renishaw Raman microscope with an excitation wavelength of 830 nm and a 20 X long working distance objective. Raman signal was collected by 180° backscattering geometry. The spectrum was recorded with an exposure time of 5 s and an average of 100 acquisitions. Electronic absorption spectra were recorded on a Analytik Jena SPECORD S100 diode-array spectrophotometer at room temperature in a 1-cm quartz cell. The emission spectra were recorded using JASCO FP-6300 spectrofluorimeter.

Fluorescence decays were recorded by time correlated single photon counting (TCSPC) method using the following set up. A diode pumped millena CW laser (Spectra Physics) 532 nm was used to pump a Ti:Sapphire rod in a Tsunami picosecond mode locked laser system (Spectra Physics). The 750 nm (8 MHz) line was taken from the Ti:Sapphire laser and passed through a pulse picker (Spectra Physics, 3980 2s) to generate 80 kHz pulses. The second harmonic output (375 nm) was generated by a flexible harmonic generator (Spectra Physics, GWU 23 ps). The vertically polarised 375 nm laser was used to excite the sample. The fluorescence emission at the magic angle (54.7°) was dispersed in a monochromator (f/3 aperture), counted by a MCP PMT (Hamamatsu R 3809) and processed through CFD, time-to-amplitude converter (TAC) and multichannel analyzer (MCA). The instrument response function for this system is ≈ 52 ps and the fluorescence decay was analyzed using the software provided by IBH (DAS-6) and PTI global analysis software.

### Computational Calculations

DFT calculations were performed using G09 package[25] and visualized using Gaussview 5.0. The ground state geometry optimization and frequency calculations were done using B3LYP functional both *in vacuo* and in a solvent field. Time-dependent DFT (TDDFT) calculations were performed under $CH_3CN$ solvent field implemented with integral equation formalism polarizable continuum model (IEFPCM). In all calculations, 6-31G(d) basis set was used for ligands, whereas LANL2DZ basis set was used to describe Re(I) metal center.[26] The output frequencies were scaled by a factor of approximately 0.975 to minimize mean actual deviation (MAD) between the experimental and the calculated spectra.[27]

### Synthesis of Ligands (L1-L4)

The ligands **L1-L4** were prepared by reaction of 2,2′-bipyridine-4,4′-dicarbaldehyde (0.30 g, 1.41 mmol), with corresponding amine (2.97 mmol) dissolved in ethanol solution. A few drops of acetic acid were added and refluxed for 3 hours. Reaction mixture was cooled to room temperature and the precipitate was filtered. The precipitate was washed with ether and dried under *vacuo* to obtain a desired product.

**L1:** The ligand **L1** was isolated as yellow solid. Yield = 0.480 g, 86%. $^1$H NMR (300 MHz, *d*$_6$-DMSO): δ ppm = 6.94 (t, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H), 8.16 (d, *J* = 3.6 Hz, 2H), 8.96 (m, 4H), 9.01 (s, 2H), 9.40 (s, 2H); IR (KBr, cm$^{-1}$): ν(OH) 3346, ν(–HC=N–) 1593; ESI-MS m/z: 395.22 $[M+H]^+$ (Calcd. 394.43).

**L2:** The ligand **L2** was isolated as yellow solid. Yield = 0.530 g, 89%. $^1$H NMR (300 MHz, *d*$_6$-DMSO): δ ppm = 2.30 (s, 6H), 6.87 (d, *J* = 8.2 Hz, 2H), 7.00 (dd, *J* = 8.2,1.5 Hz, 2H), 7.18 (d, *J* = 1.5 Hz, 2H), 8.13 (dd, *J* = 4.8, 1.5 Hz, 2H), 8.93 (m, 4H), 8.99 (s, 2H), 9.16 (s, 2H IR (KBr, cm$^{-1}$): ν(OH) 3387, ν(–HC=N–) 1595; ESI-MS m/z: 423.32 $[M+H]^+$ (Calcd. 422.48).

**L3:** The ligand **L3** was isolated as yellow solid. Yield = 0.660 g, 92%. $^1$H NMR (300 MHz, *d*$_6$-DMSO): δ ppm = 1.37 (s, 18H), 6.93 (d, *J* = 8.5 Hz, 2H), 7.24 (dd, *J* = 8.5, 2.4 Hz, 2H), 7.40 (d, *J* = 1.2 Hz, 2H), 8.19 (d, *J* = 5.1 Hz, 2H), 8.95 (d, *J* = 5.1 Hz, 2H), 9.40 (d, *J* = 4.2 Hz, 4H), 9.20 (s, 2H); IR (KBr, cm$^{-1}$): ν(OH) 3414, ν(–HC=N–) 1589; ESI-MS m/z: 507.44 $[M+H]^+$ (Calcd. 506.64).

**L4:** The ligand **L4** was isolated as yellow solid. Yield = 0.590 g, 90%. $^1$H NMR (300 MHz, *d*$_6$-DMSO): δ ppm = 7.01 (d, *J* = 8.5 Hz, 2H), 7.23 (dd, *J* = 8.5, 2.4 Hz, 2H), 7.44 (d, *J* = 2.4 Hz, 2H), 8.13 (dd, *J* = 5.1, 1.2 Hz, 2H), 8.96 (m, 4H), 9.01 (s, 2H), 9.70 (s, 2H); IR (KBr, cm$^{-1}$): ν(OH) 3358, ν(–HC=N–) 1584; ESI-MS m/z: 461.14 $[M-H]^-$ (Calcd. 463.32).

### Synthesis of complexes 1-4

The complexes **1-4** were prepared by reaction of $Re(CO)_5Br$ (0.2 g, 0.50 mmol) with ligands (**L1-L4**) (0.54 mmol) in toluene (20 mL) at reflux for 1 h. Reaction mixture was cooled to room temperature and the precipitate was filtered, washed with diethyl ether, dried and used without further purification.

**1:** The complex **1** was isolated as yellow solid. Yield = 0.335 g, 92%. $^1H$ NMR (300 MHz, $d_6$-DMSO): δ ppm = 6.94 (td, $J$ = 8.1, 1.2 Hz, 2H), 7.03 (dd, $J$ = 8.1, 1.2 Hz, 2H), 7.26 (td, $J$ = 8.1, 1.2 Hz, 2H), 7.48 (dd, $J$ = 8.1, 1.2 Hz, 2H), 8.29 (dd, $J$ = 6.0, 1.2 Hz, 2H), 9.10 (s, 2H), 9.24 (d, $J$=6.0 Hz, 2H), 9.41 (s, 2H), 9.51 (s, 2H); IR (KBr, $cm^{-1}$): ν(OH) 3468, ν(CO) 2025, 1927, 1886, ν(–HC=N–) 1618; ESI-MS m/z: 742.99 $[M-H]^+$ (Calcd. 744.57). Anal. Calcd for $C_{27}H_{21}BrN_4O_5Re$: C 43.38; H 2.83; N 7.49. Found: C 42.97; H 2.66; N 7.51.

**2:** The complex **2** was isolated as yellow solid. Yield = 0.350 g, 92%. $^1H$ NMR (300 MHz, $d_6$-DMSO): δ ppm = 2.33 (s, 6H), 6.94 (d, $J$ = 6.6 Hz, 2H), 7.10 (d, $J$ = 8.1 Hz, 2H), 7.33 (s, 2H), 8.30 (d, $J$ = 5.7 Hz, 2H), 9.12 (s, 2H), 9.26 (m, 4H), 9.42 (s, 2H); IR (KBr, $cm^{-1}$): ν(OH) 3464, ν(CO) 2025, 1928, 1892, ν(–HC=N–) 1614; ESI-MS m/z: 770.94 $[M-H]^+$ (Calcd. 772.62). Anal. Calcd. for $C_{29}H_{25}BrN_4O_5Re$: C 44.91; H 3.25; N 7.22. Found: C 44.50; H 3.15; N 7.16.

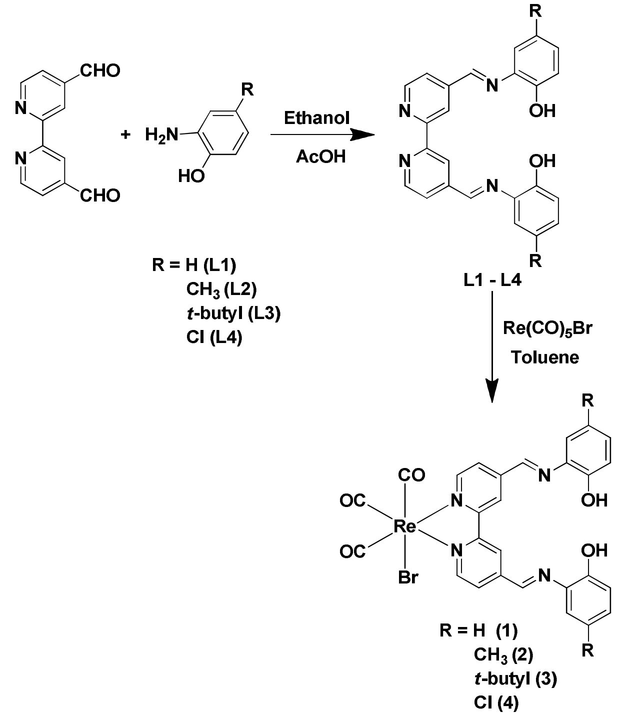
**3:** The complex **3** was isolated as yellow solid. Yield = 0.440 g, 94%. $^1H$ NMR (300 MHz, $d_6$-DMSO): δ ppm = 1.35 (s, 18H), 6.96 (d, $J$ = 8.4 Hz, 2H), 7.31 (dd, $J$ = 8.4, 2.4 Hz, 2H), 7.51 (d, $J$ = 1.4 Hz, 2H), 8.33 (d, $J$ = 5.7 Hz, 2H), 9.17 (s, 2H), 9.24 (d, $J$ = 5.7 Hz, 2H), 9.32 (s, 2H), 9.42 (s, 2H); IR (KBr, $cm^{-1}$): ν(OH) 3402, ν(CO) 2021, 1911, 1885, ν(–HC=N–) 1616; ESI-MS m/z: 855.10 $[M-H]^+$ (Calcd. 856.78). Anal. Calcd. for $C_{35}H_{37}BrN_4O_5Re$: C 48.89; H 4.34; N 6.52. Found C 49.20; H 4.24; N 6.90.

**4:** The complex **4** was isolated as yellow solid. Yield = 0.360 g, 91%. $^1H$ NMR (300 MHz, $d_6$-DMSO): δ ppm = 7.04 (d, $J$ = 8.7 Hz, 2H), 7.29 (dd, $J$ = 8.7, 2.4 Hz, 2H), 7.55 (d, $J$ = 2.4 Hz, 2H), 8.27 (dd, $J$ = 5.7, 1.2 Hz, 2H), 9.09 (s, 2H), 9.27 (d, $J$ = 5.7 Hz, 2H), 9.37 (s, 2H), 9.78 (s, 2H); IR (KBr, $cm^{-1}$): ν(OH) 3452, ν(CO) 2027, 1923, 1892, ν(–HC=N–) 1614; ESI-MS m/z: 812.86 $[M-H]^+$ (Calcd. 813.46). Anal. Calcd. for $C_{27}H_{19}BrCl_2N_4O_5Re$: C 39.72; H 2.35; N 6.86. Found: C 39.47; H 2.37; N 6.49.

## Results and discussion

### Synthesis and characterization

The synthetic route for ligands is shown in Scheme 1. The ligands **L1-L4** have been synthesized by the reaction of 2,2′-bipyridine-4,4′-dicarbaldehyde with the corresponding amine in ethanol medium to yield Schiff base type ligands. The purity of the newly synthesized ligands was confirmed by NMR, IR and mass spectral techniques. The imine linkage in the ligands was characterized by a signal at δ 9.01 ppm (–N=CH) in $^1H$ NMR spectrum (Figs S1–S4). The IR spectra of the ligands reveal the bands at 1584−1595 and 3346−3414 $cm^{-1}$, characteristic of the imine linkage and phenolic (OH) group respectively. The ESI-MS analysis showed a molecular ion peak at m/z = 395.22, 423.32, 507.44, 461.14 with the experimental isotope pattern matching the calculated values for the ligands **L1-L4**.



**Scheme 1** Synthetic route of ligands **L1-L4** and complexes **1-4**.

The rhenium(I)-carbonyl bromide complexes **1-4** were prepared by the reaction of $Re(CO)_5Br$ with the appropriate bidentate ligand **L1-L4** refluxed in toluene. The rhenium(I)-polypyridine complex, precipitated from its reaction mixture, was filtered from hot reaction mixture and then washed with hot isooctane and diethyl ether (Scheme 1). These complexes are air and moisture stable, kinetically inert. All of the newly synthesized complexes were characterized by $^1H$ NMR, IR and mass spectral techniques and further by elemental analysis. The IR spectra of the Re(I) complexes showed three intense absorption bands at 1885 – 2027 $cm^{-1}$, which correspond to three carbonyl groups. The ESI-MS analysis showed a molecular ion peak at m/z = 742.99, 770.94, 855.10, 812.86 with the experimental isotope pattern matching the calculated values for the complexes **1-4** (Figs S5–S8).

The geometry of ligand and rhenium complexes was optimized using B3LYP method with 6-31G(d) level for ligands and LANL2DZ level for rhenium(I). The optimized structures (Fig. 1) showed that rhenium has a distorted octahedral geometry and the three carbonyl groups are arranged in *facial* orientation. The calculated bond lengths and bond angles (Table 1) are consistent with other rhenium complexes having similar structure.[28] Raman spectra of Re(I) complexes show peaks in the region 1000 – 1650 $cm^{-1}$ from bpy centered modes (Figs 2 and S9). The peaks at 1027 and 1602 $cm^{-1}$ are due to ring stretching frequency. The calculated Raman spectrum, obtained from optimized geometry, matched nicely with the experimental spectrum (Fig. 2). The mean absolute deviation (MAD) between experimental peaks and calculated peaks in the region 900 – 1700 $cm^{-1}$ is < 8 $cm^{-1}$.

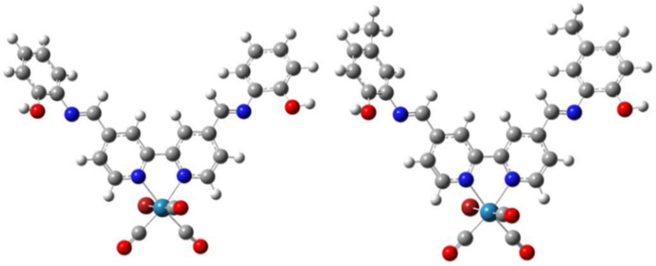


**Fig. 1** Optimized geometry of complexes **1** (left) and **2** (right).

**Table 1** Calculated bond lengths (Å) and bond angles (°) of complexes **1**–**4**.

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Re17–C18 | 1.9131 | 1.9131 | 1.9132 | 1.9137 |
| Re17–C19 | 1.9275 | 1.9278 | 1.9278 | 1.9281 |
| Re17–C20 | 1.9275 | 1.9278 | 1.9278 | 1.9281 |
| Re17–N25 | 2.2008 | 2.2004 | 2.2006 | 2.2004 |
| Re17–N26 | 2.2008 | 2.2004 | 2.2006 | 2.2004 |
| Re17-Br24 | 2.7047 | 2.7039 | 2.7037 | 2.7021 |
| N25-Re17-N26 | 74.427 | 74.422 | 74.397 | 74.425 |
| C18-Re17-Br24 | 177.284 | 177.375 | 177.430 | 177.392 |

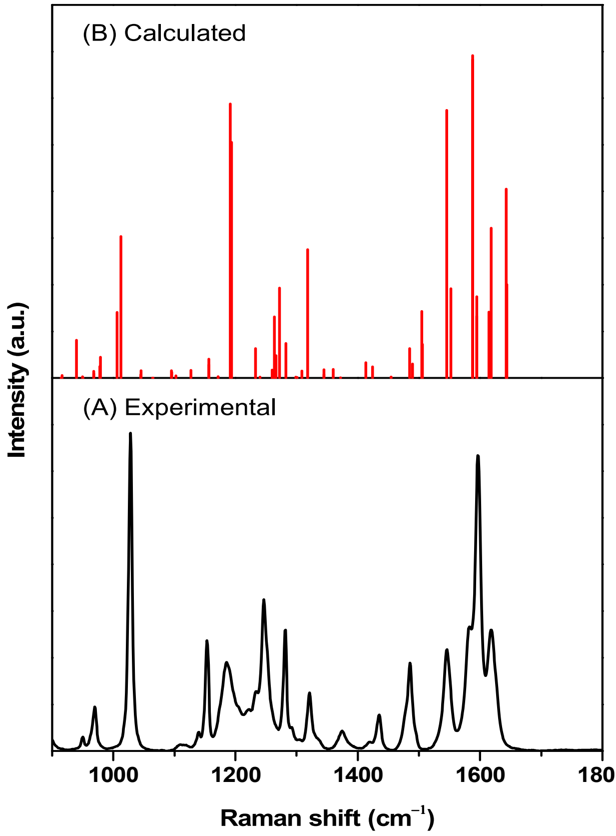


**Fig. 2** (A) Experimental Raman spectrum of complex **1** in solid state and (B) calculated spectrum.

**Absorption spectra**

The photophysical properties, the absorption, emission maxima, excited state lifetime and quantum yield of Re(I)-tricarbonyl complexes **1-4** were measured and the values given in Table 2. The absorption spectral data of ligands **L1-L4** are given in Table S1. The absorption spectra of ligands **L1-L4** and complexes **1-4** in $CH_3CN$–DMSO (99:1) showed absorption bands in the UV and visible regions. The strong absorption bands of ligands **L1-L4** at 195–224 nm is assigned to π–π* transition of bipyridine and bands in the region 350–410 nm can be assigned to charge transfer transition from phenolic moiety to bipyridine.[29] The electronic absorption spectra of complexes **1-4** have strong absorption bands in the region 194–330 nm and less intense absorption band in the region 350–470 nm (Table 2). The high energy intense band in the UV region is attributed to the ligand centered (LC) π–π* transition and it is also observed for the free ligands (Fig. S10). Upon coordination to the metal center, the low energy absorption band corresponding to charge transfer transition from phenol moiety to bipyridine moiety is red-shifted compared to free ligands. In addition to this transition, spin allowed metal to ligand charge transfer ($^1$MLCT) transition from the Re dπ– orbital to the π* orbital of the ligand [dπ (Re) → π* (ligand)] (Fig. 3) is also observed in this region. The mix of intraligand charge transfer transition and $^1$MLCT transition is evident from enhanced molar extinction coefficient seen in bands in low energy region.[30] Furthermore, these assignments are supported by DFT calculations.

**Table 2** Photophysical data of Re(I)-complexes in $CH_3CN$–DMSO (99:1) medium.

| Complex | $\lambda_{abs}$, nm ($\varepsilon_{max}$, $10^4$ $dm^3\,mol^{-1}cm^{-1}$) | $\lambda^{em}{}_{max}$, nm | Φ, $10^{-2}$ | τ (± 0.03) ns | $k_r$, $s^{-1}$ × $10^5$ | $k_{nr}$, $s^{-1}$ × $10^7$ |
|---|---|---|---|---|---|---|
| **1** | 194(7.9), 291(2.8), 397(2.5) | 606 | 0.05 | 32 | 0.2 | 3.1 |
| **2** | 195(7.1), 299(2.4), 416(2.0) | 609 | 0.04 | 29 | 0.1 | 3.4 |
| **3** | 195(8.8), 301(2.9), 415(2.3) | 611 | 0.06 | 26 | 0.2 | 3.8 |
| **4** | 197(9.3), 295(2.9), 406(1.9) | 609 | 0.14 | 19 | 0.7 | 5.2 |

The absorption maximum is sensitive to the nature of the substituent in the ligand. Introduction of a –Cl group (complex **4**) red shifts the $\lambda_{max}$ value by 9 nm from 397 to 406 nm, whereas $-CH_3$ (complex **2**) causes a large shift from 397 to 416 nm (Table 2). The position of the MLCT bands is governed by the σ- donor and π- acceptor properties of the 2,2′-bipyridyl ligands. A blue shift in this absorption band has also been observed when comparing complex **2** (416 nm) with **4** (406 nm), again in line with the change in the σ-donor ability of the ligands, in which the electron-donating ability decreases in the order: **L2** ($-CH_3$) > **L4** (–Cl). Hence, the blue shift in the absorption maximum was attributed to the increase in energy gap between the HOMO and LUMO of the ligand, causing a blue shift in the MLCT transition of complex **4** compared to complex **2**. It is likely that the more electron-rich ligand would cause a destabilization of the dπ orbital of the rhenium(I) metal centre, which would lead to a lower-energy transition.[31]

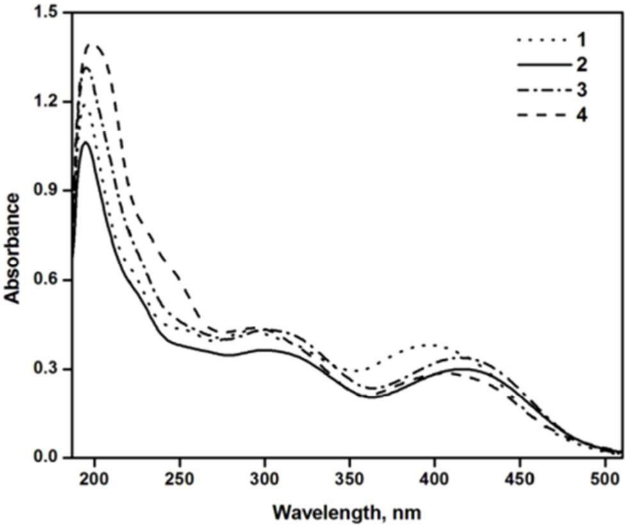


**Fig. 3** Absorption spectra of complexes **1-4** (15 μM) in $CH_3CN$–DMSO (99:1) medium.

### Time Dependent Density Functional Theory Calculations

Time dependent density functional theory (TDDFT) method was utilized to obtain the calculated absorption spectra of free ligands and rhenium complexes in $CH_3CN$ solvent field using IEFPCM model. Molecular orbital analysis of ligands (Fig. S11) showed that the highest occupied molecular orbital (HOMO) is located on phenolic moiety and lowest unoccupied molecular orbital (LUMO) is centered on bipyridine moiety. Hence, the lowest energy transition corresponds to intraligand charge transfer transition from phenolic moiety to bipyridine moiety and this supports the experimental UV-Vis absorption spectra. The calculated UV-Vis absorption spectra of complexes **1–4** are shown in Figs 4 and S12 and they match nicely with the experimental absorption spectra. The B3LYP functional underestimates the energies of MLCT and related CT transitions and hence the lowest energy transition in predicted spectra is shifted towards longer wavelength compared to experimental spectra.[26] Molecular orbital analysis of complex **1** (Fig. S13) showed that HOMO lies on both phenolic moiety and $Re(CO)_3Br$ unit and LUMO is centered on bipyridine unit. In the case of complex **2**, because of the presence of electron donating methyl group, energy of HOMO level is raised compared (Fig. 5) to that of parent complex **1** and hence HOMO is centered predominantly on phenolic moiety and LUMO is localized on bipyridine moiety (Fig. S14). The calculated absorption spectrum of **2** showed that the lowest energy transition is red-shifted compared to that of **1**, and this supports the experimentally observed results. Similar observations are found with complex **3** having electron donating *t*-butyl group as the substituent. For complex **4** with Cl substituent, HOMO is stabilized (Fig. 5) compared to the other three complexes and hence the lowest energy transition is blue shifted. Since the LUMO is also slightly stabilized, the absorption maximum of **4** lies closer to that of **1**.

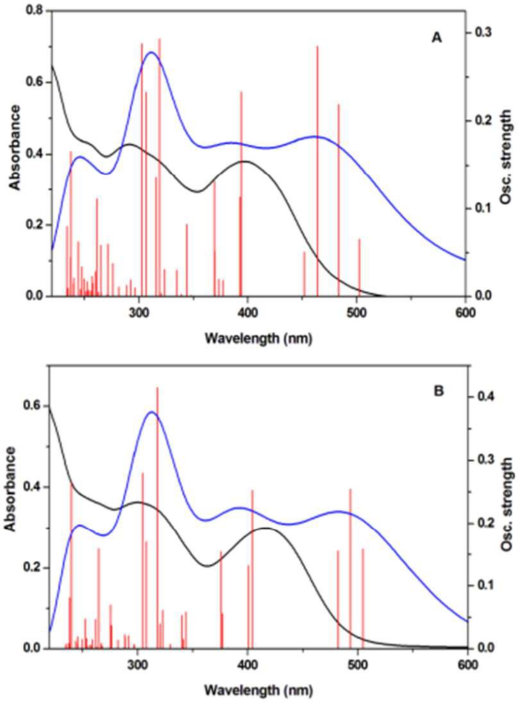


**Fig. 4** Experimental ($CH_3CN$, black) and calculated (blue) UV-Vis absorption spectra of (A) complex **1** (15 μM) and (B) complex **2** (15 μM). The oscillator strength is represented by red lines.

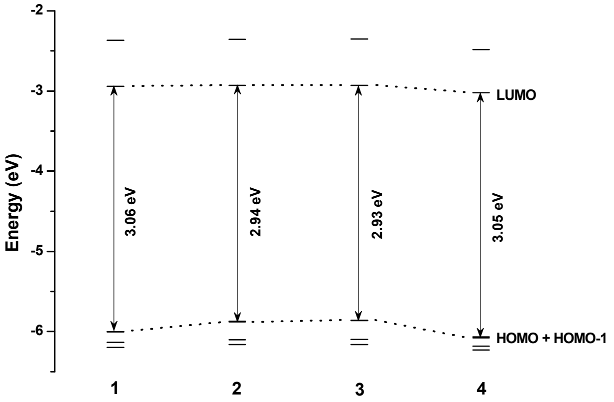


**Fig. 5** Energy level diagram of frontier orbitals of **1–4**. Energy level of HOMO and HOMO-1 are close and they are merged.

### Emission spectra

The emission spectra for the complexes **1-4** were recorded and the data given in Table 2. Fig. 6 shows the emission spectra of complexes **1-4** in $CH_3CN$–DMSO (99:1, v/v) medium at room temperature. Upon excitation at $^1$MLCT absorption region, the $^3$MLCT emission was observed for complexes **1-4** in the region 606–611 nm in $CH_3CN$ at RT.[32] Introduction of electron donating substituent such as $-CH_3$, *t*-butyl at the phenolic moiety causes red shift of luminescence maximum. Luminescence wavelength is in the order of **1** < **2** < **3**. These data indicate that more electron donating substituent at the phenolic moiety leads to more efficient ICT and thus bipyridine moiety should act as an electron acceptor.[33] The quantum yields of complexes **1-4** were calculated using $[Ru(bpy)_3]^{2+}$ ($\Phi_{em}$ = 0.062 in $CH_3CN$) as the standard, and the values were found to be $5.0 \times 10^{-4}$ for **1**, $4.0 \times 10^{-4}$ for **2**, $6.0 \times 10^{-4}$ for **3**, $1.4 \times 10^{-3}$ for **4** and the lifetimes of these complexes are in the range of 19 – 32 ns. The six-coordinated rhenium(I) complex with three carbonyl groups as co-ligands exhibited octahedral geometry with low-spin $5d^6$ electronic configurations. The three carbonyl groups contribute π–back bonding to the metal centre significantly, and thus, the energy gap between the Re(I) *d*-orbitals and the π* orbital of the ligand is reduced and low energy emission and low luminescence quantum yield is observed.[34] For complexes **1**–**4**, the non-radiative decay is in the order of $10^7$ $s^{-1}$. Meyer and coworkers reported non-radiative decay of rhenium(I)-polypyridyl complexes in the order $10^6 – 10^8$ $s^{-1}$.[35]

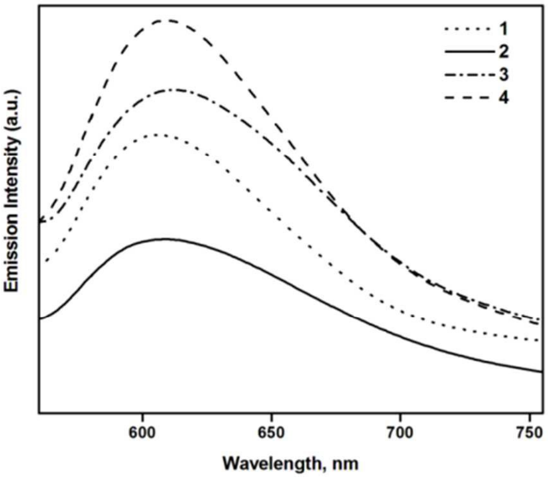


**Fig. 6** Emission spectra of complexes **1-4** (15 μM) in $CH_3CN$–DMSO (99:1) medium.

### Absorption spectral titration

To investigate the binding properties of complexes **1-4** toward metal ions, hydrated nitrate salts of $Na^+$, $K^+$, $Ag^+$, $Sr^{2+}$, $Ba^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$ $Hg^{2+}$, iodide salt of $Cu^+$ and perchlorate salt of $Fe^{2+}$ in $CH_3CN$–DMSO (99 : 1 v/v) were studied by UV-vis absorption spectral measurements. A substantial change in the absorption spectrum can be noticed only on the addition of $Cu^{2+}$ ion to the acetonitrile solution of complexes **1-4** (Figs S15–S18). Conversely, little absorption spectral change was observed on the addition of other metal ions. The addition of $Cu^{2+}$ ion to the solution of complex **1** results in the red shift of LC absorption to the tune of 7 nm from 194 to 201 nm, of 38 nm in the band at 291 nm and a rapid decrease in the absorption at 397 nm (Fig. 7). An isosbestic point is clearly observed at 255, 265, 286 and 361 nm, suggesting the chemical interaction between complex **1** and $Cu^{2+}$ ion. Similar results were observed when other Re(I) complexes are treated with different concentration of $Cu^{2+}$ ion (Figs S19–S21).

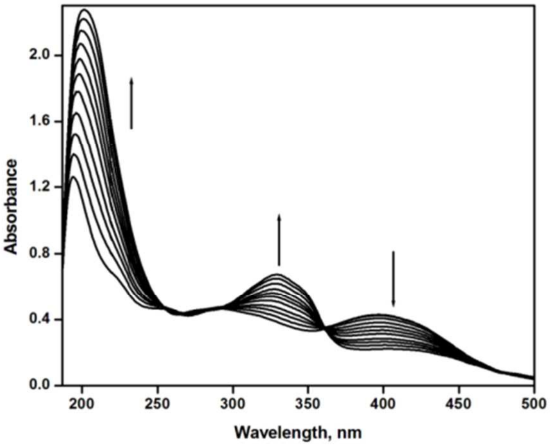


**Fig. 7** Absorption spectral changes observed with complex **1** (15 μM) with increasing concentration of $Cu^{2+}$ ion in $CH_3CN$ medium. $[Cu^{2+}]$ = (0-50 μM).

The binding constant of complexes **1-4** with $Cu^{2+}$ ion is calculated through the Benesi-Hildebrand equation[36] and the values are collected in Table 3. The model Benesi-Hildebrand plot is shown in Fig. S22. The absorption spectral changes indicate the strong binding of $Cu^{2+}$ ion with the Re(I) complexes and the binding constants are in the range of $1.1\times10^3$ – $6.0\times10^3$ $M^{-1}$.

**Table 3** Binding constant values of complexes **1-4** with $Cu^{2+}$ using absorption ($K_a$) and emission ($K_b$) spectral techniques and limit of detection (LOD).

| Complex | $K_a \pm 0.2$, $M^{-1}$ | $K_b \pm 0.2$, $M^{-1}$ | LOD, M |
|---|---|---|---|
| 1 | $1.1 \times 10^3$ | $2.2 \times 10^3$ | $7.6 \times 10^{-6}$ |
| 2 | $4.5 \times 10^3$ | $6.0 \times 10^3$ | $5.8 \times 10^{-6}$ |
| 3 | $5.5 \times 10^3$ | $7.3 \times 10^3$ | $4.3 \times 10^{-6}$ |
| 4 | $6.0 \times 10^3$ | $7.9 \times 10^3$ | $2.8 \times 10^{-6}$ |

### Luminescence spectral titration

The binding behavior of complexes **1-4** towards different metal cations has also been investigated by the emission spectral studies. The selective binding of complexes **1-4** with $Cu^{2+}$ ion among all other metal ions is confirmed by recording the emission spectrum of Re(I) complex in the absence and presence of the metal ions. A significant emission enhancement in the intensity as well as in the quantum yield was observed only in presence of $Cu^{2+}$, among all the other metal ions used (such as $Na^+$, $K^+$, $Ag^+$, $Sr^{2+}$, $Ba^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^+$, $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$ and $Hg^{2+}$). The emission maximum, quantum yield, lifetime, radiative and non-radiative rate constants of complexes **1**–**4** in the presence of $Cu^{2+}$ ion are collected in Table 4. The red shift of the emission maxima could be explained by the fact that the binding of the cations to imine ligand would decrease σ-donating ability and stabilize the π* orbital of the bipyridine ligand and hence decreased the emission energy.[37] The influence of metal ions on Re(I)-

complexes **1-4** is shown in Figs S23–S26. The relative change in the emission intensity of Re(I)-complexes **1-4** with different metal ions are shown in Figs S27–S30.

**Table 4** Emission maximum, quantum yield (Φ), lifetime (τ), radiative ($k_r$) and non-radiative ($k_{nr}$) rate constants of Re(I) complexes **1-4** in the presence of $Cu^{2+}$ ion.

| Compounds | $\lambda^{em}_{max}$, nm | Φ $10^{-2}$ | τ (± 0.03) ns | $k_r$, $s^{-1}$ × $10^5$ | $k_{nr}$, $s^{-1}$ × $10^7$ |
|---|---|---|---|---|---|
| 1 + $Cu^{2+}$ | 612<br>(606) | 1.22<br>(0.05) | 40 (32) | 3.0<br>(0.2) | 2.5<br>(3.1) |
| 2 + $Cu^{2+}$ | 614<br>(609) | 1.16<br>(0.04) | 40 (29) | 2.9<br>(0.1) | 2.5<br>(3.4) |
| 3 + $Cu^{2+}$ | 611<br>(611) | 1.88<br>(0.06) | 36 (26) | 5.2<br>(0.2) | 2.7<br>(3.8) |
| 4 + $Cu^{2+}$ | 613<br>(609) | 1.29<br>(0.14) | 32 (19) | 4.0<br>(0.7) | 3.1<br>(5.2) |

Values in the parenthesis represent the values in the absence of $Cu^{2+}$ ion

Complex **1** alone displayed a weak luminescence emission band at 606 nm with a negligible luminescence quantum yield of 0.05 × $10^{-2}$, when it was excited at 397 nm. The luminescence intensity of complex **1** at *ca*. 606 nm increases with a gradual addition of $Cu^{2+}$ ion. A ~32-fold increase in the luminescence intensity (Fig. 8), with a slight red-shift, was observed in the presence of $Cu^{2+}$ ion [Φ value of complex **1** increases from 0.05 × $10^{-2}$ to 1. 22 × $10^{-2}$ in the presence of $Cu^{2+}$ ion]. Similar results were observed for complexes **2-4** (Figs S31–S33). The high fluorescence enhancement factor of complexes **1-4** upon the addition of $Cu^{2+}$ ion shows great potential for application to the fluorescent sensing of $Cu^{2+}$ at a low concentration level. Thus the complexes **1-4** behave as an "off-on" type of luminescence probe towards $Cu^{2+}$.

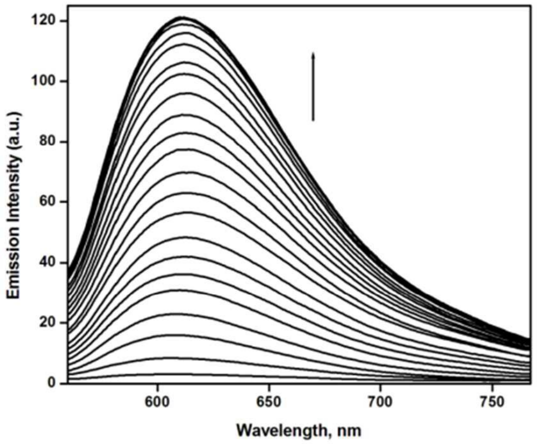
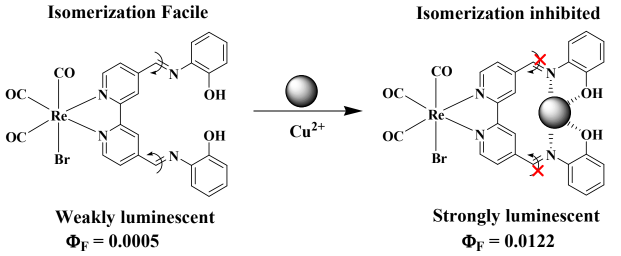


**Fig. 8** Emission spectral changes observed with complex **1** (15 µM) with increasing concentration of $Cu^{2+}$ ion in $CH_3CN$ medium. [$Cu^{2+}$] = (0-200 µM).

The significant increase of luminescence intensity and quantum yield of **1-4** in the presence of $Cu^{2+}$ ion can be explained as follows: Complexes **1-4** are weakly luminescent in part due to isomerization of the C=N bond in the excited state.[38] However, this isomerization can be inhibited by the effective binding of suitable metal ions leading to stability and regaining the luminescence. Interestingly, complexation of Re(I) complexes **1-4** with $Cu^{2+}$ ion restricts the isomerization of C=N moiety so that their luminescence is drastically increased (Scheme 2). Sheng *et al.*[39] have shown that the coumarin-based imine was non-emissive due to the fast deactivation through a non-radiative pathway as a result of C=N isomerization. But, in the presence of $Cu^{2+}$ ion, enhancement of luminescence intensity is observed due to the inhibition of the C=N isomerization process upon complexation with $Cu^{2+}$ ion.[39] This luminescence enhancement may be explained with the aid of mechanism proposed in Scheme 2.



**Scheme 2** Proposed binding mechanism between complex **1** and $Cu^{2+}$ ion.

The binding constants (K) of complexes **1-4** with $Cu^{2+}$ ion were calculated from the emission data using modified Benesi-Hildebrand equation.[36] The model Benesi-Hildebrand plot is shown in Fig. S34 and the values are collected in Table 3. The luminescence spectral changes indicate the strong binding of $Cu^{2+}$ ion with Re(I) complexes and the binding constants are in the range of 2.2 × $10^3$ – 7.9 × $10^3$ $M^{-1}$. These values are in close agreement with the values calculated from the absorption spectral data confirming the reliability of these values. Furthermore, the Job's plot is applied for the determination of the stoichiometric ratio between the Re(I) complex and $Cu^{2+}$ ion (Fig. S35) and this plot reveals 1:1 complex formation between $Cu^{2+}$ ion and Re(I) complexes. The observed binding constants in the range of $10^3$ $M^{-1}$ is low to extend the application of this system for sensing Cu(II) ion in biological system. The low binding constant may be attributed to the binding of Cu(II) to a ligand 2,2′-bipyridine carrying two phenolic moieties which is already strongly coordinated to Re(I) ion. The coordination of Cu(II) to two phenolates and two imine centres leads to the formation of a complex similar to Cu(II)-salen complex. This coordination of Cu(II) to two O and two N centres leads to the formation of a new absorption peak at 329 nm (Fig. 7), which can be due to the formation of Cu(II)-salen-like complex. Though the binding affinity is in the millimolar range this Re(I) complex is an interesting and important sensor system as it is able to sense Cu(II) ion selectively compared to other similar metal ions. As far we know there is only one report on the Re(I)-polypyridyl complex to serve as sensor for Cu(II) ion.[14c] But in this study the binding constant value is not reported. The change of emission intensity can be ascribed to the amount of $Cu^{2+}$ ion bound to the Re(I) complexes and the detection limit was calculated with the equation:[40] detection limit = $3S_b/m$ where $S_b$ is the standard deviation of the blank and m is the calibration sensitivity, which corresponds to the slope of the linear part of the calibration curve (Fig. S36). $S_b$ was determined from the emission intensity of the sensor solution in the absence of metal ions by performing a series of five measurements. The detection limit values are collected in Table 3.[41] The obtained detection limit was found to be in the range of $2.8 \times 10^{-6} – 7.6 \times 10^{-6}$. Kaur and Kumar[42] reported that the dansyl-anthracene dyads show selective recognition towards $Cu^{2+}$ ion amongst alkali, alkaline earth and other heavy metal ions using absorbance and fluorescence spectral techniques, and the detection limit is $10 \times 10^{-6}$ M. Ma and co-workers[43] reported iridium(III) complex-based chemosensor bearing the 5,6-bis(salicylideneimino)-1,10-phenanthroline ligand receptor, which exhibited color change from colorless to yellow and a visible turn-off luminescence response upon the addition of Cu(II) ions. Indeed, our system showed luminescence turn-on response, which is preferred over turn-off response.

### Luminescence decay studies

The interaction of complexes **1-4** with $Cu^{2+}$ ion was also investigated using the time-resolved luminescence technique. The time-resolved luminescent decay profiles of complexes **1-4** in the presence of $Cu^{2+}$ ion are shown in Figs S37–S40. The lifetime of complexes **1-4** is in the range of 19 – 32 ns and the values collected in Table 4. The presence of $Cu^{2+}$ ion increases the excited state lifetime of complexes **1-4** to 32 – 40 ns. The values of rate constant for radiative ($k_r$) and non-radiative ($k_{nr}$) processes have been calculated using $\tau$ and $\Phi_{em}$ values and given in Table 4. The increase in the quantum yield and lifetime values for complexes **1-4** in the presence of $Cu^{2+}$ ion is attributed to the increase in the radiative decay and decrease in the non-radiative decay when compared to the values for the free complexes. It is suggested that binding of $Cu^{2+}$ ion with a luminophore serves to rigidify the receptor and thus inhibit vibrational and rotational relaxation modes of non-radiative decay leading to an enhancement in the emission properties of the luminophore.[44] These observations in the luminescence properties are in good agreement with the steady-state luminescence spectral measurements and make the complexes **1-4** act as a selective sensor for $Cu^{2+}$ ion.

## Conclusion

In summary, a series of four new tricarbonyl rhenium(I) complexes comprising hydroxyl and imine group attached to 2,2′-bipyridine ligands have been synthesized and characterized by various spectroscopic techniques. These complexes were found to serve as fluorescent ‘turn-on’ chemosensor for $Cu^{2+}$ ion. The excited state lifetime and quantum yield of Re(I) complex is also significantly increased on the addition of $Cu^{2+}$ ion. It exhibits high selectivity and sensitivity towards $Cu^{2+}$ over other metal ions in $CH_3CN$ solution and the formation of a rigid structure between imine and $Cu^{2+}$ ion inhibits the C=N isomerization, leading to luminescence enhancement of the Re(I) complexes.

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## Notes and references

[a]School of Chemistry, Madurai Kamaraj University, Madurai – 625 021, India
[b]Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India
[c]Institute of Chemistry, Academia Sinica, Taipei, 115 Taiwan

E-mail: rajagopalseenivasan@yahoo.com (S. Rajagopal)
Tel: 91-452-2458246; Fax: 91-452-2459139

E-mail: umapathy@ipc.iisc.ernet.in (S. Umapathy)
Tel: 91-80-22932595; Fax: 91-80-23601552

E-mail: ptsekaran@yahoo.com (P. Thanasekaran)
Tel.: +886-2-27898518; fax: +886-2-27831237

Electronic Supplementary Information (ESI) available: $^1H$ NMR spectra of Ligands **L1-L4**, ESI-MS spectra of complexes **1-4**, Raman spectrum of complex **3** in solid state, UV-vis spectra of ligands **L1-L4**, MO pictures of ligand **L1** and complexes **1** and **2**, experimental and calculated UV-Vis absorption spectra of complexes **3** and **4**, UV-vis and emission spectral changes observed with complex **1-4** with increasing concentration of $Cu^{2+}$ ion, Benesi-Hildebrand plot and modified Benesi-Hildebrand plot for complex **1**, Relative emission intensity changes of complex **1-4** with different metal ions, Calibration curve of complex **4** for $Cu^{2+}$, Job’s plot for complex **1** with $Cu^{2+}$ ion, Time resolved luminescence decay of complexes **1-4** in the presence of $Cu^{2+}$ ion.

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