Indian Journal of Chemistry
Vol. 58A, June 2019, pp. 621-628

Luminescent rhenium(I) complex of azo ligand based on quinoline: Synthesis, characterization and computational investigations

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Received 10 December 2018; revised and accepted 22 May 2019

Reaction of 7-(quinolin-8-yldiazenyl)quinolin-6-ol, HL, (where H represents the dissociable proton upon complexation) based on quinoline with [Re(CO)$_5$Cl] in toluene afforded brown colored product of composition [Re(CO)$_3$L]. The mononuclear Re(I) complex has been characterized unequivocally. Molecular structure of the complex *fac*-[Re(CO)$_3$L] has been confirmed by single-crystal X-ray diffraction. The complex exhibited excellent photoluminescence behavior in solution state. The ground and excited-state geometries and absorption properties of the Re(I), complex has been further examined by DFT and TDDFT methods.

Keywords: Mononuclear Re(I) complex, X-ray structure, Photoluminescence, Life time, Computational studies

The synthesis and photophysical investigation of the transition metal complexes of heavier metal ions with d^6 electronic configurations, such as rhenium(I)[1], ruthenium(II)[2], osmium(II)[3], rhodium(II)[4] and iridium(III)[5] are still an active area in the field of photo-induced molecular devices[6-9]. This is due to their extensive applications in the field of energy conversion[10,11], sensing[12-14], and molecular electronics[15-17]. Apart from the other heavy metal complexes, Re(I) complexes of general formula *fac*-[Re(CO)$_3$]$^+$ are of growing interest due to their excellent luminescent properties and the origin has been attributed to the triplet metal Re(I) to ligand charge transfer (^{3}MLCT) excited state. More interestingly, the Re(I) complexes have potential efficacy owing to their unique combination of chemical stability, strong visible absorption, excited state reactivity, photo-redox chemistry and catalytic properties. The behavior of Re(I) complexes had attracted attention to exploit these materials for solar energy conversion, light emitting devices, electron transfer reaction, reduction of CO$_2$ in a homogeneous solution as well as at the electrode surfaces, chemi- or electro chemiluminescence detectors and in the field of bioimaging[18-27]. In this perspective, the utilization of chelating ligand having quinoline nitrogen as donor atom represents an important target when coordination of rhenium(I) metals is taken into consideration. The distinct coordinating ability of the nitrogen of the chromophoric quinoline ring induces the formation of the stable metal complex with a concomitant increase in their luminescent properties. The photophysical properties can be fine-tuned by modifying both the metal center and the ligand structure[28].

Keeping the aforementioned observations in mind, we have designed and synthesized mononuclear rhenium(I) quinolato complex with a tridentate (N, N, O donor) ligand having azo(N=N) function. The complexes are characterized by IR, UV-vis, ^{1}H NMR spectroscopic techniques. The complex formation has been authenticated on the basis of single crystal X-ray studies. The photophysical properties of the complex were also investigated. The ligand as well as the complex has different emissive nature and shows remarkably different quantum yield compared to the similar type of chromophoric moiety established by the author[29] earlier. It is interesting to note that the introduction of a nitrogen center in place of a carbon bought a huge jump in the quantum yield of the complex. To get a better insight into the geometry and the electronic structure, geometry optimization of the ground state and optical properties of this complex, density functional theory (DFT) and time dependent density functional theory (TD-DFT) studies have also been included.

Materials and Methods

[Re(CO)$_5$Cl] (98% used) was purchased from Aldrich Chemical Co. All the chemicals and solvents were analytically pure and used without further purification. Infrared spectra were recorded on a Perkin-Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. ^{1}H-NMR spectra was recorded on a Bruker FT 400 MHz instrument. For NMR spectra, $CDCl_3$ was used as the solvent using TMS as an internal standard. UV-vis experiments were performed on a Perkin–Elmer LAMBDA 25 spectrophotometer and the fluorescence experiment was performed using Horiba FluroMax-4 fluorescence spectrometer and a fluorescence cell of 10 mm path length. Elemental analysis (C, H, and N) was performed on a Perkin-Elmer 2400 series II analyzer. Quantum yield of the complex [$Re(CO)_3L$] was determined in freeze-pump-thaw-degassed solution of the complex by a relative method using quinine sulphate as the standard [Φ_{std}= 0.54 (at 298 K) in 0.1 M H_2SO_4 at λ_{ex}= 350 nm]. Time-correlated single photon counting (TCSPC) measurement was carried out for the luminescence decay of complex [$Re(CO)_3L$] in acetonitrile. For TCSPC measurement, the photoexcitation was made at 480 nm using a picoseconds diode laser (IBH Nanoled-07) in an IBH Fluorocube apparatus. The fluorescence decay data were collected on a Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBH DAS6 software.

Computational details

The geometrical structure of the singlet ground state (S_0) were optimized using the density functional theory (DFT)[32] method at the RB3LYP levels of theory[33]. The geometry of the mononuclear Re(I) complex was fully optimized in solution phase. The absorption spectral properties of the mononuclear Re(I) complex based on the optimized ground state geometry structure was computed using the time dependent density functional theory (TDDFT)[34] approach in dichloromethane associated with the conductor-like polarizable continuum model (CPCM)[35]. In the calculation, the quasi-relativistic pseudo potentials of Re atoms proposed by Hay and Wadt[36] with 14 valence electrons (outer-core [($5s^25p^6$)] electrons and the ($5d^6$) valence electrons) were employed, and a "double-ξ" quality basis set LANL2DZ was adopted as the basis set for Re atoms. The 6-31G+g basis set was used for the C, H, N and O atoms for the optimization of both the ground state geometries. All the calculations were performed using the Gaussian 09W software package[37]. The Gauss Sum 2.1 program[38] was used to calculate the molecular orbital contributions from groups or atoms.

Crystallographic studies

Single Crystals of [$Re(CO)_3L$] complex was grown by slow diffusion of hexane in dichloromethane solution at 25 °C. Data were collected on a Brucker SMART CCD diffractometer using Mo-Kα monochromatic (λ=0.71073 nm). Structure solutions were performed using Shelx 97 PC version program[39]. Full matrix least square refinements on F2 were performed using SHELXL-97 program[40]. All the non-hydrogen atoms were refined anisotropically using full-matrix least squares method. Hydrogen atoms were included for structure factor calculations after placing them at calculated positions. Atomic coordinates and isotropic thermal parameters of [$Re(CO)_3L$] are given in Table 1.

Synthesis

Synthesis of HL

8-amino quinoline (0.1 mmol) was dissolved in 0.25 M hydrochloric acid (1.0 mL) and cooled to –5 °C. Then the solution was diazotized with the dropwise addition of 12 M sodium nitrite solution (1.0 mL) solution at –5 °C. Excess nitrous acid was then quenched by adding a small amount of urea to the solution at –5 °C. Meanwhile, 6-hydroxy quinoline (0.1 mmol) was dissolved in 80 mM sodium hydroxide solution (5 mL). The solution was then cooled to –5 °C. The cold solution of the diazonium salt was added dropwise to this solution at –5 °C.

Table 1 — Atomic coordinates and isotropic thermal parameters of [($Re(CO)_3L$] complex

Chemical formula	$C_{21}H_{11}N_4O_4Re$
Formula weight/ $gmol^{-1}$	569.54
Crystal system	Monoclinic
space group	P 21/n (No. 14)
a/ Å	9.2011(8)
b/ Å	18.8104(17)
c / Å	10.7107(9)
α/ deg	90
β/ deg	93.587(4)
γ/ deg	90
λ/ Å	0.71073
V/ Å^3	1850.1(3)
F(000)	1088
Z	4
T/ K	296(2)
D/ mgm^{-3}	2.045
μ/ mm^{-1}	6.606
R1(all data)	0.0934
wR2[$I > 2\sigma(I)$]	0.2661
GOF	1.587

The mixture was stirred at –5 °C for 1 h and at room temperature overnight. The dark red precipitation appeared on the acidification by the dilute acetic acid. The precipitate was separated on filtration and washed several time with water and dried under vacuum.

Yield: 102 mg (70%). Elemental Anal. Calcd for $C_{18}H_{12}N_4O$: C, 71.99; H, 4.03; N, 18.66. Found: C, 71.90; H, 3.95; N, 18.70. IR (KBr pellets, cm^{-1}): ν(N=N) 1485. ^{1}H NMR $CDCl_3$: δ (ppm), *J* (Hz):11.65(s, 1H), 9.39(dd, 1H), 8.77 (dd, 1H), 8.50-8.42 (m, 3H) 7.94(t, 2H), 7.77(t, 1H), 7.65-7.61(m, 1H), 7.50-7.47(m, 1H).

Synthesis of $[Re(CO)_3L]$ complex

To a stirred solution of HL (25 mg, 0.08 mmol) in 20 mL of dry toluene, $[Re(CO)_5Cl]$ (20 mg, 0.055 mmol) and triethylamine (3/4 drops) were added and then the resulting mixture was refluxed for 4–5 h under argon atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane and was purified by thin layer chromatography on silica plate with toluene/CH_3CN (95:5) as the eluent. A brown band was separated and the complex was extracted from silica with dichloromethane and methanol. The brown solid, obtained upon evaporation of the solvent, was recrystallized from dichloromethane-hexane. Yield: 27 mg (90%). Elemental Anal. Calcd for $C_{21}H_{11}N_4O_4Re$: C, 44.29; H, 1.95; N, 9.84. Found: C, 44.35; H, 1.85; N, 9.88. IR (KBr pellets, cm^{-1}): ν(facial) CO 2013 and 1895; ν(N=N) 1484. ^{1}H NMR $CDCl_3$: δ (ppm), *J* (Hz):9.04 (dd, 1H), 9.03(d, 1H), 8.68 (dd, 1H), 8.31 (dd, 1H) 8.20(dd, 1H), 7.89(d, 1H), 7.69–7.63(m, 2H), 7.53(dd, 1H), 7.44(dd, 1H) 7.03(d, 1H).

Results and Discussion

Ligand

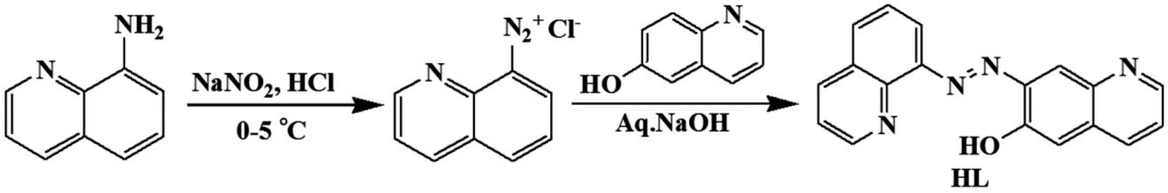
The ligand was prepared by the diazo-coupling reaction of 6-hydroxyquinoline with 8-amino quinoline[30] (Scheme 1).

Complex

Reaction of the preformed HL ligand with the commercially available precursor $[Re(CO)_5Cl]$ in 1:1 stoichiometric ratio in dry toluene under refluxing condition afforded solid complex of the composition $[(Re(CO)_3L]$ in excellent yield (Scheme 2). Its structure was confirmed by X-ray crystallography.

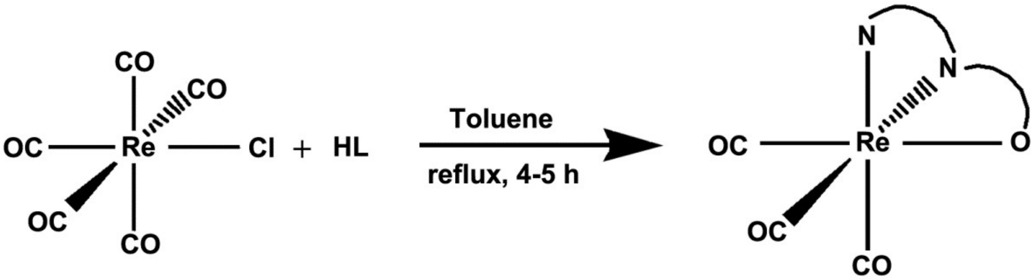
Characterization

The ligand HL and complex $[(Re(CO)_3L]$ were well characterized by IR, ^{1}H NMR techniques (Supplementary Data, Fig. S1-S4). The HL ligand displayed the characteristic[28] ν N=N at 1485 cm^{-1}. The ν N=N of the ligand HL slightly shifts to lower frequency (1484 cm^{-1}) after formation of the



Synthesis of 7-(quinolin-8-yldiazenyl)quinolin-6-ol ligand

Scheme 1



Schematic representation for the synthesis of the [(Re(CO)3L] complex

Scheme 2

[(Re(CO)$_3$L] complex representing the coordination to the metal centre. The δ OH (11.65) of the HL ligand disappeared after the formation of the complex. The ^{1}H NMR spectral features for the aromatic protons of the ligand HL and complex [(Re(CO)$_3$L] matched well with the composition and structure. These data are collected in experimental section.

Crystal structure description

Single crystal of rhenium(I) complex suitable for structure determination was grown by slow evaporation from the acetonitrile solution. The crystallographic data collection was done in 2θ range 55° and refinement parameters are given in Table 1; selected bond lengths and angles are given in Table 2. The perspective view of [(Re(CO)$_3$L] is shown in Fig. 1.

In complex [(Re(CO)$_3$L], the geometry around rhenium(I) is distorted octahedral, where the mono anionic deprotonated ligand (L) binds in a tridentate (N,N,O) fashion forming the mononuclear chelate complex. The Re(I) center is coordinated by quinoline nitrogen [N(3)], azo nitrogen[(N(1)], deprotonated hydroxyl [OH] and three carbonyl ligands. The carbonyl ligands are arranged in a facial mode and the remaining equatorial sites are occupied by quinoline nitrogen and phenoxo oxygen of the coordinated ligand. The remaining axial site is occupied by azo(N=N) nitrogen. The Re-C (CO) bond distances trans to nitrogen atoms of the quinoline and azo(N=N) moiety are slightly longer than Re-C(CO) bond distance trans to the phenoxo group and this can be attributed to the π-accepting ability of nitrogen atoms than oxygen.

Geometry optimization, electronic structure

To understand the ground state geometry, electronic structure of the mononuclear Re(I) complex [(Re(CO)$_3$L], geometry optimization was performed in solution phase assuming a singlet ground state (S = 0, t$_2$g^6). The geometry utilized for the ground state optimization is based on crystal structure parameter of the complex [(Re(CO)$_3$L] without ligand modification. The optimized bond lengths and bond angles of the complex [(Re(CO)$_3$L] are given in Table 3.

The optimized geometrical structure of the [(Re(CO)$_3$L] complex at ground (S$_0$) state is shown in Fig. 2. The geometry around the Re(I) center in the mononuclear [(Re(CO)$_3$L] complex is distorted octahedral where all the three CO ligands are in facial position. The optimized parameters of the complex [(Re(CO)$_3$L] are well matched with the X-ray crystal structure data. The calculated Re-C and Re-O bond

Table 2 — Selected Bond Lengths (Å) and Angles (degree) for [(Re(CO)$_3$L] complex

Bond Lengths (Å)			
Re1-O1	2.128(6)	C5-O1	1.300(8)
Re1-O1	2.128(6)	C10-N3	1.307(9)
Re1-C20	1.934(7)	C17-N3	1.390(8)
Re1-C21	1.919(8)	Re1-C19	1.907(9)
N1-N2	1.289(8)	Re1-N3	2.216(6)
C4-N2	1.375(8)	C16-N1	1.423(9)
Bond Angles (°)			
C21-Re1-C19	88.6(3)	C20-Re1-O1	94.6(3)
C21-Re1-C20	87.1(3)	C21-Re1-N3	170.8(3)
C19-Re1-C20	87.8(3)	C19-Re1-N3	86.4(3)
C21-Re1-N1	99.1(3)	C20-Re1-N3	100.4(3)
C19-Re1-N1	100.5(3)	N1-Re1-N3	74.3(2)
C20-Re1-N1	169.7(3)	O1-Re1-N3	93.4(2)
C21-Re1-O1	91.3(3)	C5-O1-Re1	119.1(5)
C19-Re1-O1	177.7(3)		

Table 3 — Selected optimized geometrical parameters for [(Re(CO)$_3$L] in the ground (S$_0$) at B3LYP levels

Bond Lengths (Å)			
	S$_0$		S$_0$
Re1-C12	1.913	Re1-N8	2.155
Re1-C15	1.928	Re1-O2	2.163
Re1-C37	1.930	C6-O2	1.313
Re1-N5	2.226	N8-N9	1.304
Bond Angles (°)			
C15-Re1-C37	90.13	C15-Re1-O2	88.92
C37-Re1-N5	97.89	Cl5-Re1-N9	99.00
C37-Re1-C12	90.33	C15-Re1-C12	89.44
C37-Re1-O2	95.25	O2-C6-C39	123.74
N5-Re1-N9	73.85	C39-N8-N9	119.76
N5-Re1-O2	95.16	N9-C10-C38	113.14

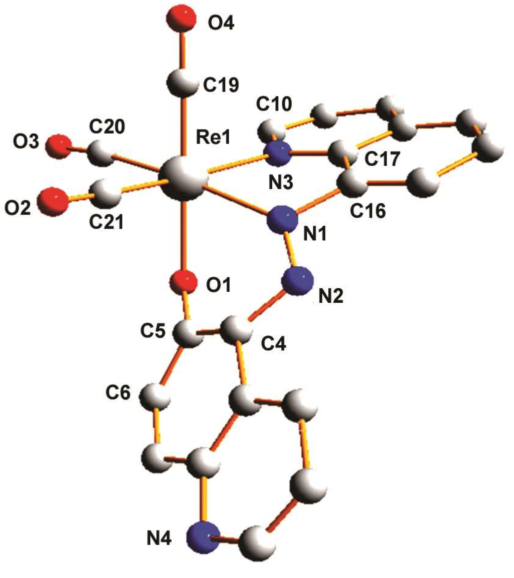


Fig. 1 — Perspective view of *fac*-[(Re(CO)$_3$L] complex. Hydrogen atoms are omitted for clarity.

distances occur at 1.92 Å and 2.16 Å respectively and Re-N (quinoline N) and Re-N (azo N) bond distance arise near 2.226 Å and 2.155 Å for the complex [(Re(CO)$_3$L] which are almost same with the experimental values. The calculated N=N (azo) bond distance (~1.304 Å) in the complex [(Re(CO)$_3$L] remains almost unchanged with the experimental result. These observations clearly demonstrate that there are no significant changes of the ligand structure in the mononuclear Re(I) complex. The isodensity plot from H–5 to L+5 for [(Re(CO)$_3$L] is shown in Fig. 3.

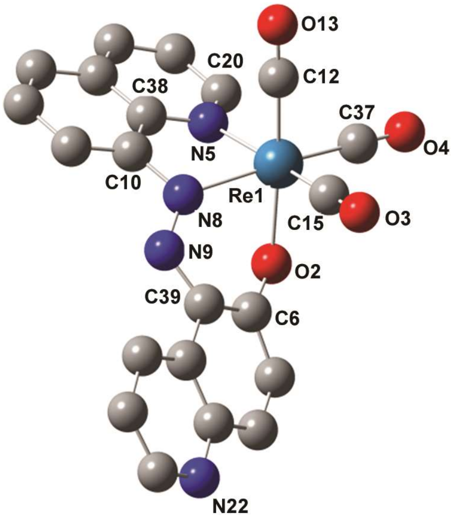


Fig. 2 — Optimized molecular view of [(Re(CO)$_3$L] complex (Re: cyan, N: blue, O: red, C: grey. All hydrogen atoms are omitted for clarity.

The energy and compositions of selected frontier molecular orbital of the [(Re(CO)$_3$L] complex in singlet ground state (S$_0$) are listed in Table 4. The energy difference between HOMO and LUMO of the complex [(Re(CO)$_3$L] equals to 2.51 eV. The highest occupied orbitals (HOMO) are mainly consisted of π orbital of hydroxy quinoline attached with azo (N=N) bond to the rhenium d orbital with some contribution of π orbital of CO molecule. The electron density in H–1 is mainly localized on the rhenium centre with slight contribution of the π orbital of CO molecule. The energy of HOMO-3 and HOMO-4 are almost degenerate (energy difference ~ 0.09 eV in the complex [(Re(CO)$_3$L]. The electron density of the LUMO (L) and L+1 of complex [(Re(CO)$_3$L], originates from the π orbital of azo ligand HL.

TDDFT calculation and electronic spectra

The ground state electronic spectra of both the ligand HL and complex [(Re(CO)$_3$L] were recorded in dichloromethane solution at room temperature. The ligand HL displayed characteristic UV-Vis spectra in dichloromethane solution with an absorption maximum near 347 nm and complex shows moderately intense peak at 595 nm and high intense peak at 340 nm (Fig. 4).

To get deep insight into the electronic transitions, TDDFT/B3LYP/CPCM calculation on the optimized geometry of the complex [(Re(CO)$_3$L] has been performed in dichloromethane. In the TDDFT

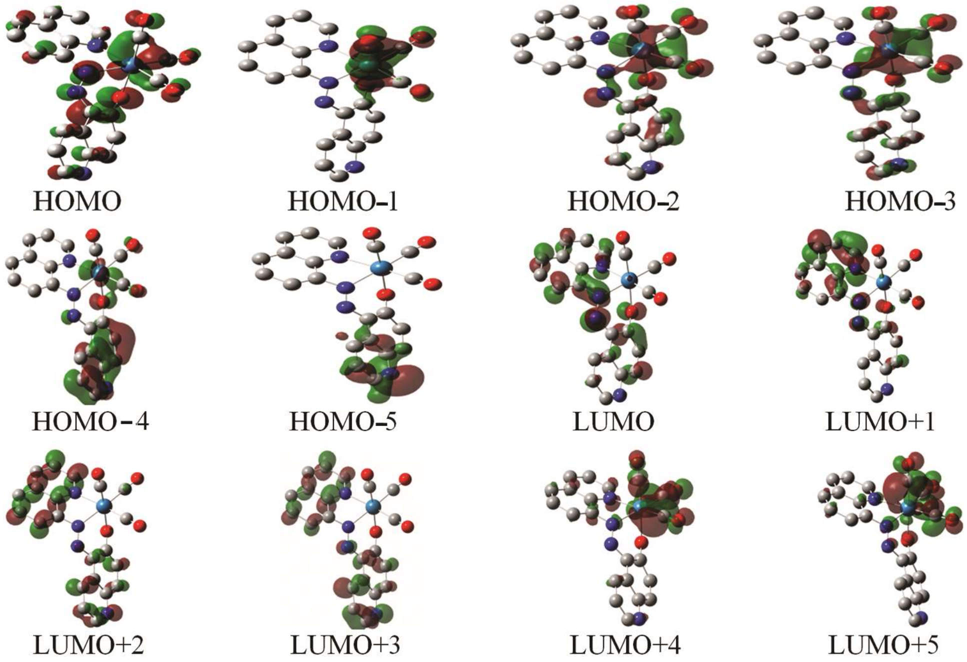


Fig. 3 — Isodensity plot of frontier orbitals of [(Re(CO)$_3$L] complex.

Table 4 — Energy and composition of selected molecular orbitals of [(Re(CO)$_3$L]

MO	Energy (eV)	% of composition					Main bond types
		Re	CO	Azo	Ligand		
					Hq	Aq	
LUMO+5	–1.09	3	62	4	4	7	π^*(Aq) + π^*(CO)
LUMO+4	–1.26	24	60	0	4	14	p(Re) + π^*(CO) + π^*(Aq)
LUMO+3	–1.63	23	1	5	51	42	p(Re) + π^*(Hq) + π^*(Aq)
LUMO+2	–1.75	1	3	3	33	58	π^*(Hq) + π^*(Aq)
LUMO+1	–2.76	3	4	11	13	70	π^*(Hq) + π^*(Aq) + π^*(azo)
LUMO	–3.35	3	2	30	32	34	π^*(Hq) + π^*(Aq) + π^*(azo)
HOMO	–5.86	21	14	15	37	12	d(Re) + π(Hq) + π(aq) + π(CO) + π(azo)
HOMO–1	–6.46	59	27	0	10	4	d(Re) + π(CO) + π(Hq)
HOMO–2	–6.58	45	21	7	25	3	d(Re) + π(CO) + π(Hq) + π(azo)
HOMO–3	–7.01	47	18	6	25	4	d(Re) + π(CO) + π(Hq) + π(azo)
HOMO–4	–7.1	14	5	3	73	4	d(Re) + π(CO) + π(Hq)
HOMO–5	–7.21	1	0	1	98	0	π(Hq)

Hq = Hydroxy quinoline, Aq = Amino quinoline

Table 5 — Main calculated optical transition for the complex [(Re(CO)$_3$L] with composition in terms of molecular orbital contribution of the transition, vertical excitation energies, and oscillator strength in acetonitrile

Composition	Excitation Energy(eV)	Osc.Strength (*f*)	Assign	λ_{exp} (nm)
H→ L	2.0421 (607 nm)	0.1512	^{1}MLCT/^{1}ILCT	595
H→ L+2	4.00(352 nm)	0.0904	^{1}MLCT/^{1}ILCT	340
H–5→ L			^{1}ILCT	
H–1→L+1			^{1}MLCT	

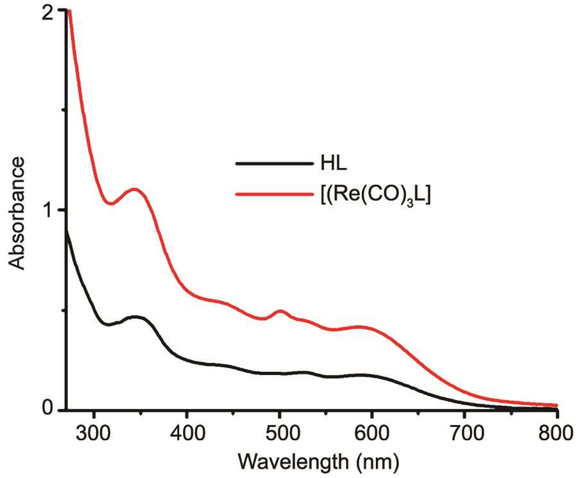


Fig. 4 — Absorption spectra of HL and [(Re(CO)$_3$L] complex.

calculation we have moderately intense transition at 607 nm (f = 0.1512) corresponds to H→ LUMO having ^{1}MLCT character with little ^{1}ILCT (Table 5)[30]. The highest energy band with maxima at 309 nm for complex [(Re(CO)$_3$L] can rationally be assigned to an admixture of metal-to-ligand charge transfer (^{1}MLCT) transition and spin-allowed π→ π*(ligand-centered, ^{1}ILCT) transitions[30].

Emission spectral properties

The emission property of the ligand HL and [(Re(CO)$_3$L] complex were measured in dichloromethane solution. The π conjugated chromophore containing ligand, HL displayed high intense emission maxima at 395 nm and a very low intense emission at 558 nm on excitation at 335 nm. The emission intensity of Re(I) complex can be attributed to the triplet metal Re(I) to ligand charge transfer(^{3}MLCT) excited state[31].

On the other hand, the complex [(Re(CO)$_3$L] exhibited excellent photoluminescence near 405 nm on excitation at 350 nm (quantum yield (Φ) ca.0.105) (Fig. 5). Moreover the time resolved luminescence spectra also provides the evidence to recognize the decay process and the emissive nature of the complex.

Life time data is recorded for [(Re(CO)$_3$L] complex at room temperature in dichloromethane solution when excited at 350 nm. The observed luminescence decay fit with bi-exponential decay nature of the complex [Re(CO)$_3$L] (Fig. 6). The fluorescence life time (τ), radiative (k_r) and nonradiative (k_{nr}) decay rate constant of the complex Re(CO)$_3$L] are collected in Table 6.

Table 6 — The photophysical parameters of the complex [(Re(CO)$_3$L] in dichloromethane solution at room temperature

Sample	τ_1, ns	τ_2, ns	τ_{av}	Φ	k_r,ns^{-1} (±5% error)	k_{nr}, ns^{-1} (±5% error)
fac-[(Re(CO)$_3$L]	2.2 (43%)	8.7 (57%)	2.9	0.105	0.017	0.15

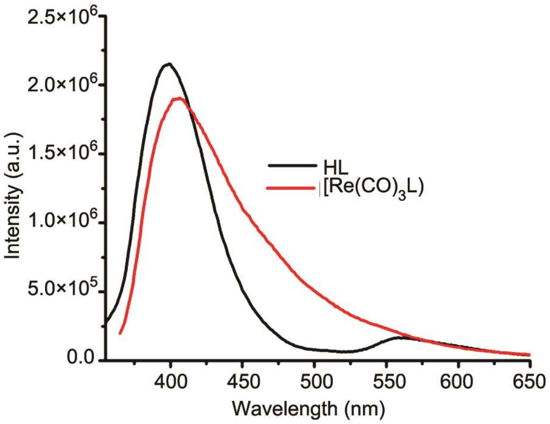


Fig. 5 — Emission spectra of HL (λ_{ex}= 335nm, λ_{em}= 395 nm) and complex (λ_{ex}= 350 nm, λ_{em}=406 nm) in dichloromethane solution, at room temperature.

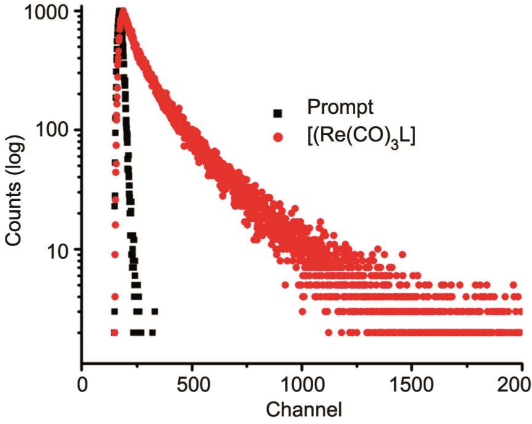


Fig. 6 — Time-resolved Fluorescence lifetime decay of [Re(CO)$_3$L] complex.

Conclusions

In summary, the mononuclear Re(I) complex could be prepared upon reaction of the azo ligand HL based on quinoline moiety with appropriate metal substrate. The structure of the complex was authenticated by X-Ray crystallography analysis. The complex exhibited excellent luminescent properties with high quantum yield. The present work also investigated the ground state geometry and absorption properties of [Re(CO)$_3$L] complex by DFT and TDDFT methods.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_58A(06)621-628_SupplData.pdf.

Acknowledgement

D S thanks the RUSA 2.0 for research fellowship and S.P.P. thanks the DST-SERB (New Delhi) for research fellowship. The necessary laboratory and infrastructural facility are provided by the Department of Chemistry, Jadavpur University.

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