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Synthesis, Characterization and DFT studies of Complexes Bearing [Re(CO)₃]⁺ Core and Reactivity Towards Cyanide ion

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Abstract:

Mononuclear rhenium(I) complexes having fac-[Re(CO)₃]⁺ core of general formula fac- $[Re(CO)_3(L)Cl]$ have been synthesized in excellent yield by reacting $[Re(CO)_5Cl]$ with L₁ and L_2 in a ratio of 1:1 in toluene under inert atmosphere. Here L_1 and L_2 are N-((quinolin-2yl)methylene)-9H-fluoren-2-amine N-((anthracen-10-yl)methylene)quinolin-8-amine and respectively. Spectroscopic measurements such as NMR, ESI-MS and IR spectroscopy were used to ensure the formations of desired complexes. Molecular structures of fac-[Re(CO)₃(L₁)Cl] and fac-[Re(CO)₃(L₂)Cl] were confirmed by single-crystal X-ray diffraction. The ligands are emissive whereas the metal complexes are weak emitter. A remarkable change in absorption as well as emission behavior was observed in complex 2 upon addition of cyanide ion. Interruption in intraligand charge transfer in complex 2 is the probable reason for the obvious change in spectral response of the same. ¹H NMR titration was performed as the evidence of the previously stated fact. The ground and excited-state geometries, absorption properties of rhenium(I) complexes were examined by DFT and TDDFT methods. The natural transition orbital (NTO) and analysis reveal the nature of excitations.

Keywords: Schiff base, rhenium(I), spectroscopy, anion sensor, DFT

1. Introduction

Rhenium tricarbonylchloro complexes with N^N coordinating Schiff base ligands having d⁶ electronic configuration is one of the widely studied area in coordination chemistry due to its interesting photophysical properties [1-2] such as room-temperature luminescence from lowlying tunable metal to ligand charge transfer (MLCT) excited states [3-9], solar-energy conversion [10-12], OLED and sensor development [13-18], and biological labeling [19-20]. These imine-based rhenium complexes having [Re(CO)₃]⁺ core show interesting optical behavior in presence of toxic anions. It is possible to create a highly potential receptor molecule by varying ligand architecture with the photoactive rhenium(I) metal center. A few groups of researchers have shown the sensing properties of rhenium(I) complex by hydrogen bonding $(NH \cdots X)$ followed by deprotonation [21-25]. Anion sensing mechanism by deprotonation of O-H bond has also been reported [26]. But, anion recognition through the addition of an anion into the imine bond is rare. Cyanide ion is a very toxic anion which comes into environment through its use in pharmaceutical industries, insecticides, fertilizers, plastic manufacturing processes, extraction of metals, electroplating industries etc [27-30]. It is necessary to replace the conventional methods of testing for cyanide such as titration, distillation, chromatography or potentiometry as they are expensive, laborious and time consuming. Therefore, there is still a need to develop more robust and less laborious testing methodologies for cyanide. In this context, the complexes of rhenium(I) are suitable. It has proven that $Re(CO)_3$ ⁺ core potentially influence the imine based complex to detect cyanide ion selectively among other anions [31]. So, the main focus of this paper is the successful synthesis of two rhenium complexes with N^N coordinating two different Schiff base ligands. We have also described the details of synthetic procedures of these mononuclear complexes and the characterization is done by various spectroscopic techniques and single crystal X-Ray diffraction study. The reactivity of these complexes towards various anions has also been studied. To describe the ground and excited state behavior of the Re(I)-diimine complexes, the contribution of the fundamental computational chemistry such as DFT/TDDFT [32] and NTO analysis is indispensable to get better insight into the geometry, electronic structure and optical properties, TDDFT calculations of several excited states have been performed.

2. Experimental Section

2.1. Materials

 $Re(CO)_5Cl$, 2-Aminofluorene, 9-Anthraldehyde, 8-Aminoquinoline, Quinoline-2carboxaldehyde were purchased from Sigma Aldrich. All solvents and chemicals are analytically pure. All the reactions with $Re(CO)_5Cl$ were carried out under argon atmosphere.

2.2. Physical measurements

Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Micromass QTOF YA 263 mass spectrometer. IR spectra were observed and obtained with a Perkin–Elmer L-0100 spectrophotometer with KBr disk. ¹H NMR spectra were measured on Bruker FT 500 MHz spectrometer in CDCl₃and DMSO solvent. By Perkin–Elmer LAMBDA 25 spectrophotometer UV–Vis spectra were investigated. The emission data were collected on a Horiba FluroMax-4 fluorescence spectrometer. Quantum yields of the complexes were determined in freeze-pump-thaw-degassed solutions of the complexes using quinine sulfate in the same solvent as the standard [Φ_{std} = 0.54 (at 298 K) in 0.1M H₂SO₄ at λ_{ex} = 350 nm] by usual method. The quantum yields were calculated using eq 1,

$$\Phi_{\rm r} = \Phi_{\rm std} \frac{A_{\rm std}}{A_{\rm r}} \frac{I_{\rm r}}{I_{\rm std}} \frac{\eta_{\rm r}^2}{\eta_{\rm std}^2}$$
(1)

Where, Φ_r and Φ_{std} are the quantum yields of unknown and standard samples, A_r and A_{std} (<0.1) are the solution absorbance's at the excitation wavelength (λ_{ex}), I_r and I_{std} are the integrated emission intensities, and η_r and η_{std} are the refractive indices of the solvent. Time–correlated single–photon–counting (TCSPC) measurements were carried out for the luminescence decay of complexes in dichloromethane. On a Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBH DAS6 software, the fluorescence decay data were investigated.

2.3. Computational details

The geometrical structures of the ground-state of the selected complexes were optimized by the DFT method with B3LYP exchange correlation functional approach [33-34]. The geometry of the complexes was fully optimized in solution phase without any symmetry constraints. There was a good agreement between the theoretical and experimental structures. On the basis of the optimized ground state geometry structure, the absorption property in dichloromethane (DCM)

and methanol (MeOH) media was calculated by time-dependent density functional theory (TDDFT) approaches associated with the conductor-like polarisable continuum model (CPCM) [35]. We computed the lowest 50 singlet – singlet transition and results of the TD calculations were qualitatively very similar. The TDDFT approach had been demonstrated to be reliable for calculating spectra properties of many transition metal complexes [36-37]. Due to the presence of electronic correlation in the TDDFT (B3LYP) method it can yield more accurate electronic excitation energies. Hence TDDFT had been shown to provide a reasonable spectral feature for our complex of investigation.

In the calculation, the quasi relativistic pseudo potentials of Re atoms proposed by Hay and Wadt 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. For H we used 6-31(g) basis set and the 6-31+G(d) basis set for C, N, O, and Cl atoms for the optimization of the ground state geometries. Figures showing MOs and the difference density plots were prepared by using the Gauss View 5.1 software. All the calculations were performed with the Gaussian 09W software package [38]. Gauss Sum 2.1 program [39] was used to calculate the molecular orbital contributions from groups or atoms.

2.4. Crystallographic studies

The single crystal suitable for X-ray crystallographic analysis of the complex was obtained by slow evaporation of acetone solution of the complex. The X-ray intensity data were collected on Bruker AXS SMART APEX CCD diffractometer (Mo K α , $\lambda = 0.71073$ Å) at 293 K. The detector was placed at a distance 6.03 cm from the crystal. Total 606 frames were collected with a scan width of 0.3° in different settings of φ . The data were reduced in SAINTPLUS [40] and empirical absorption correction was applied using the SADABS package [41]. Metal atom was located by Patterson Method and the rest of the non-hydrogen atoms were emerged from successive Fourier synthesis. The structures were refined by full matrix least-square procedure on F². All non-hydrogen atoms were refined anisotropically. Two large electron density value near the rhenium metal centre (_refine_diff_density_max 9.428 for Q1) and (_refine_diff_density_max 7.11 for Q2) was located at the end of the refinement cycle. However, the connectivity and other broad structural features of the complex were refined to a reasonable degree with respect to data quality and are undoubtedly correct. All calculations were performed using the SHELXTL V 6.14 program package [42]. Molecular structure plots were drawn using

the Oak Ridge thermal ellipsoid plot (ORTEP) [43]. The CCDC numbers are 1921556 and 1921582 for complexes **1** and **2** respectively. Relevant crystal data is given in Table 1.

	1	2
Formula	C ₂₆ H ₁₆ ClN ₂ O ₃ Re	$C_{28}H_{18}C_{13}N_2O_3Re$
M _r	626.06	722.99
Crystal system	Triclinic	Triclinic
Space group	P -1	P -1
<i>a</i> / Å	6.9438(7)	10.0610(17)
b / Å	9.0741(8)	10.9620(19)
<i>c</i> / Å	18.6879(17)	13.023(2)
α /°	99.723(3)	86.860(13)
β /°	98.947(3)	77.069(13)
γ /°	100.024(3)	69.510(12)
$V/\text{\AA}^3$	1121.94(18)	1310.9(4)
Ζ	2	2
$D_{\rm calcd}/{\rm g~cm^{-3}}$	1.853	1.832
μ/mm^{-1}	5.566	4.974
$\theta^{\prime \circ}$	2.253-27.482	1.521-26.855
T/K	273 K	296
Reflns collected	5133	5387
R1, ^a wR2 ^b $[I >$	0.1052, 0.2766	0.0680, 0.1797
$2\sigma(I)$]		
GOF on F^2	1.117	1.032

Table 1Crystal data and structure refinement parameters for complexes 1 and 2

 ${}^{a}R1 = \Sigma \left| \left| F_{o} \right| - \left| F_{c} \right| \right| / \Sigma \left| F_{o} \right|. {}^{b} wR2 = \left[\Sigma \left[w \left(F_{o}^{2} - F_{c}^{2} \right)^{2} \right] / \Sigma \left[w \left(F_{o}^{2} \right)^{2} \right] \right]^{1/2}$

2.5. Syntheses of Ligand

(9H-Fluoren-2-yl)-quinolin-2-ylmethylene-amine (L₁): 2-Aminofluorene (500 mg, 2.75 mmol) was dissolved in 20 ml ethanol followed by addition of 2-quinolinecarboxaldehyde (433.15 mg, 2.75 mmol). The resultant mixture was stirred for 2 hours. A yellow precipitate was obtained and it was collected under suction filtration and washed with ethanol. Yield: 70 %, ¹H NMR (CDCl₃, 300 MHz): δ 8.86 (s, 1H); 8.35 (d, 1H, J = 15); 8.17 (dd, 1H, J= 9), 8.67 (d, 1H, J = 9), 8.43 (d, 1H, J = 9), 8.30 (d, 1H, J= 8), 8.17 (t, 1H, J = 12), 7.94 (t, 1H, J = 8), 7.6-7.3 (Ar, 5H), 3.91(9H of fluorine, 2H).¹³C NMR {(CDCl₃, 500 MHz, δ (ppm)}: 193.05, 150-110; Anal. calcd for C₂₃H₁₆N₂: C, 86.22, H, 5.03, N, 8.74. Found: C, 86.68, H, 5.44, N, 8.62; ESI-MS (CH₂Cl₂): m/z 321.159[M+H]⁺. IR (cm⁻¹): v (imine C=N): 1614.

3-Ethylidene-2-methylene-2,3-dihydro-naphthalen-1-ylmethylene)-quinolin-8-yl-amine

(L₂): 9-Anthraldehyde (500 mg, 2.25 mmol) was dissolved in 20 ml ethanol followed by addition of 8-Aminoquinoline (396.46 mg, 2.25 mmol). The resultant mixture was refluxed for 2 h with the addition of 1 drop of acetic acid. A yellow precipitate was obtained and it was collected under suction filtration and washed with ethanol. Yield: 80%, ¹H NMR (CDCl₃, 500 MHz): δ 8.88(s, 1H); 8.39 (d, 1H, J=10); 8.23 (q, 2H, J=10), 7.85-7.74 (m, 4H), 7.60 (q, 3H, J=10), 7.38 (t, 1H, J=5). ¹³C NMR {(CDCl₃, 500 MHz, δ (ppm)}: 160-111; Anal. calcd for C₂₄H₁₆N₂: C, 86.72, H, 4.85, N, 8.43. Found: C, 86.49, H, 4.46, N, 8.28; ESI-MS (CH₃CN): m/z 333.190 [M+H]⁺; IR (cm⁻¹): v (imine C=N): 1610.

2.6. Complex Synthesis

fac-[**Re**(**L**₁)(**CO**)₃**Cl**],1. Re(CO)₅Cl (50mg, 0.147mmol), **L**₁ (47.09 mg,0.147 mmol) were taken in 30 ml toluene and then the resulting mixture was refluxed for 10 h. After cooling to room temperature, the solvent was removed under reduced pressure. A red coloured solid was obtained. The product on recrystallization from dichloromethane–hexane afforded red coloured crystals. Yield: 60%, ¹H NMR (DMSO-d₆, 500 MHz): δ 9.7 (s, 1H); 9.03 (d, 1H, J=10); 8.71(d, 1H, J=10), 8.4 (d, 1H, J=10), 8.33 (d, 1H, J=10), 8.19 (q, 2H, J=10), 7.99(t, 2H, J=10), 4.09 (s, 2H).¹³C NMR {(DMSO-d₆, 500 MHz, δ (ppm)}: 196, 206 (CO), 171-118; Anal. calcd for C₂₆H₁₆N₂O₃ClRe : C, 49.88, H, 2.58, N, 4.47. Found: C, 49.58, H, 2.17, N, 4.42; ESI-MS (CH₂Cl₂): m/z 642.15 [M+H]⁺. IR (cm⁻¹): v (CO): 1881, 1920 and 2019. *fac*-[Re(L₂)(CO)₃Cl] 2. Re(CO)₅Cl (50mg, 0.147mmol), L₂ (48.86 mg, 0.147 mmol) were taken in 30 ml toluene and then the resulting mixture was refluxed for 10 h. After cooling to room temperature, the solvent was removed under reduced pressure. A red colored solid was obtained. The product on recrystallization from dichloromethane–hexane afforded red colored crystals. Yield: 68%, ¹H NMR (CDCl₃, 500 MHz): δ 10.28 (s, 1H); 9.36(d, 1H, J=5), 8.70(s, 1H), 8.60(s, 1H), 8.26-7.45(m, 3H); ¹³C NMR {(CDCl₃, 500 MHz, δ (ppm)}: 196, 198, 207 (CO), 173-120; Anal. calcd for C₂₇H₁₆N₂O₃ClRe : C, 50.82, H, 2.53, N, 4.39. Found: C, 50.67, H, 2.08, N, 4.30; ESI-MS (CH₂Cl₂): m/z 661.10 [M+Na]⁺. IR (cm⁻¹): v (CO): 1879, 1919 and 2013.

3. Result and discussion

3.1. Synthesis

The Schiff base ligands L_1 and L_2 are synthesized according to the conventional method by the condensation reaction of an aldehyde and amine (Scheme 1) and are used as neutral bidentate N, N donor ligands towards Re(I) metal center. These complexes consist of two different fluorophore segments i.e. 2-Aminofluorene and 9-Anthraldehyde, which are able to show interesting photophysical properties. It is to be noted that the choice of such ligands helps us to achieve our goal in the context of synthesis of mononuclear rhenium(I) complexes with interesting optical properties.



Scheme1. Schematic representation of the synthesis of ligands L_1 and L_2

The stoichiometric reaction of $[\text{Re}(\text{CO})_5\text{Cl}]$ with ligands \mathbf{L}_1 and \mathbf{L}_2 in 1:1 ratio in boiling toluene under argon atmosphere afforded red colored complexes of composition $[\text{Re}(\text{CO})_3(\text{L}_1)\text{Cl}]$ and $[\text{Re}(\text{CO})_3(\text{L}_2)\text{Cl}]$ respectively in excellent yields (Scheme 2). The recrystallization of these complexes from dichloromethane-hexane layer provided red crystals. X-ray crystallographic study confirms the formation of the complexes **1** and **2**.



Scheme 2. Schematic representation of the synthesis of complexes 1 and 2

3.2. Characterization

The ligands L_1 , L_2 and the corresponding complexes [Re(CO)₃(L₁)Cl] and [Re(CO)₃(L₂)Cl] were characterized satisfactorily by IR, ESI-MS and ¹H NMR spectroscopy. The IR spectra of the complexes exhibited the characteristic metal carbonyl stretching frequency in the range of 1880-2023 cm⁻¹, which is due to the presence of *fac*-[Re(CO)₃]⁺ core having C₃v symmetry. The IR data of all these compounds are given in the experimental section. The comparison between the IR stretching frequencies of ligands and corresponding complexes has shown in Fig. (S13 & S14).

The ¹H NMR spectra of the complexes and ligands was recorded in $CDCl_3$, DMSO-d₆. The complexes are diamagnetic and display well resolved NMR spectra in $CDCl_3$ and DMSO-d₆ solution and the spectral data are given in the experimental section. The assignment of NMR peaks is based on the intensity and spin-spin splitting pattern. A singlet due to azomethine

hydrogen atom observed at ~ 10 ppm in both the complexes. The active methylene hydrogens (- CH_2) of complex 1 is observed at 4.091 and in ligand L_1 it is observed at 3.91 ppm which depicts the downfield shift of methylene proton due to complexation. The ¹H NMR spectral features for the aromatic protons of the ligands and complexes matched well with the composition and structure.

3.3. Crystal structure description

The molecular structures of the complexes fac-[Re(CO)₃(L₁)Cl], **1** and fac-[Re(CO)₃(L₂)Cl], **2** were determined by single-crystal X-ray diffractometer. Both the complexes crystallize in the *P*-*I*space group. The selected bond distances and bond angles for **1** and **2** are listed in Table S3, and the molecular views are shown in Fig. 1. In these two complexes, ligands behave as N, N coordinating neutral ligand. Here, the geometry around the Re(I) metal center is distorted octahedral. It can be characterized by C26-Re-N2 bond angle (167.5) in **1** and C27-Re-N1 bond angle (174.7) in **2**. The Re-Cl bond is relatively longer (~ 0.3 Å) than other Re-N and Re-C bonds. N1-Re-N2 bond angles are 74.3° and 75.5° for **1** and **2** respectively, which gives rise to cyclic five membered ring in both complexes. The carbonyl ligands are arranged in a facial mode and the remaining equatorial sites are occupied by pyridyl nitrogen and nitrogen coming from other part of the ligand moiety. The remaining axial site is occupied by a chlorine atom.



Figure 1. ORTEP plot of complex 1 (left) and complex 2 (right) showing essential numbering and H atoms are omitted for clarity. Solvent (dichloromethane) is omitted in complex 2.

3.4. Photophysical study of ligand

The absorption spectra of the ligands L_1 and L_2 were recorded in acetonitrile at room temperature (given in Fig 2). L_1 and L_2 show absorption bands of lowest energy at 361 and 390 nm respectively which are attributed to the $n \rightarrow \pi^*$ transition. The higher energy absorptions were observed in UV region at 272 nm and 257 nm for L_1 and L_2 respectively. The higher energy absorption of these ligands arises in the UV region at 272 nm and 257 nm respectively. These bands can be reasonably assigned as an admixture of $\pi \rightarrow \pi^*$ transitions and weaker $n \rightarrow \pi^*$ transition which are submerged under a stronger $\pi \rightarrow \pi^*$ transition.



Figure 2. Absorption spectra of L_1 and L_2 in acetonitrile keeping the concentration (c = 2×10^{-5} M).

To get better agreement with the experimental photophysical values, TDDFT calculations were performed for the ligands L_1 and L_2 on the basis of the optimized geometry both in the singlet ground state (S₀) and excited state (S₁) in acetronitrile solvent. The absorption energies associated with their oscillator strengths, the main configurations and their assignments calculated using the TDDFT method and the S₀ geometry for L_1 and L_2 is discussed here (Fig. 3). The energy difference between HOMO and LUMO of L_1 and L_2 is 3.3 eV and 2.8 eV respectively. The calculated absorption bands are in good agreement with the experimental result. These absorption bands can be assigned to intramolecular charge transfer (ICT) band with some rearrangement of electron density from fluorene moiety to quinoline moiety in L_1 and from anthracene moiety to quinoline moiety in L_2 .



Figure 3. Frontier molecular orbitals involved in the UV–Vis absorption spectrum of ligands L_1 and L_2 (for clarity we considered the molecular orbital with the higher value of CI (<0.5) for the appropriate transition).

The emission property of the ligands is measured in acetonitrile solution. Ligands L_1 and L_2 show emission band at 405 nm and 470 nm when excited at 360 nm and 390 nm respectively. A relatively larger stokes shift is observed in case of L_2 (80 nm) than L_1 (45 nm). The emission intensity of L_2 is also greater than L_1 . The ligands L_1 and L_2 were emitters with quantum yields 0.03 and 0.11 respectively. The luminescence parameters for all the ligands are listed in Table 2. The emission spectra of ligands are shown in Fig. 4.



Figure 4. Experimental emission spectra of the ligands L_1 ($\lambda_{\text{excitation}} = 360 \text{ nm}$) and L_2 ($\lambda_{\text{excitation}} = 390 \text{ nm}$) having concentration, $c = 2 \times 10^{-5}$ M in acetonitrile at room temperature.

Time-resolved luminescence spectra are proved to be an important tool to understand the decay process and the emissive nature of the compounds. Thus time-resolved luminescence spectra were recorded for L_1 , L_2 . The emission lifetime (τ), radiative (k_r) and nonradiative (k_{nr}) decay rate constants were collected in Table 2. The lifetime of L_1 ($\tau_1 = 0.17$ ns and $\tau_2 = 1.5$ ns) is relatively higher than that of L_2 ($\tau_1 = 0.48$ ns and $\tau_2 = 0.15$ ns). All these ligands display biexponential decay nature. Two closely lying singlet excited states are mainly responsible for this. The ligands consist of two organic units linked by C=N bond, in which one part behaves as donor and another as acceptor. While photoexcitation, electron transfer occurs from donor to acceptor which creates charge separation resulting in generation of an opposite force that twists the donor acceptor junction. This intramolecular twisted excited state gives rise to the formation of TICT (twisted intramolecular charge transfer) state. The bi exponential decay of these two ligands with very small red shifted emission depicts the existence of TICT state.

Compound	$\lambda_{excitation}$	$\lambda_{emission}$	Quantum	$K_{nr} \times 10^8 \text{ s}^{-1}$	$K_r \times 10^7 \text{ s}^{-1}$	τ_1 ns	τ_2 ns
	(nm)	(nm)	Yield (Φ)				
L_1	360	405	0.03	6.2	2.5	0.17	1.54
L_2	390	470	0.11	18	24	0.48	0.15
2 -CN	437	505	0.19	1.3	3.05	1.83	6.29

Table 2 Photophysical parameters of the mononuclear complexes in acetonitrile solution at room temperature

3.5. Photophysical study of complex

The absorption spectra of the mononuclear complexes (1 and 2) are recorded in acetonitrile at room temperature (given in Fig 5). As compared to the ligands, the corresponding complexes show bathochromic shift in the longer wavelength region. This fact illustrates that the incorporation of rhenium(I) actually responsible for the bathochromic shift. The low lying absorption bands of these complexes ~ 400 nm are assigned as metal to ligand charge transfer (MLCT) band [Re($d\pi$) \rightarrow ligand π^* orbital]. The higher energy absorption band with high molar absorption value ~ 250 nmcan be assigned as the intraligand charge transfer band (ILCT) and weaker contribution of MLCT band. Table 3 confirms the usual assignments of all the absorption bands for complexes 1 and 2.



Figure 5. Absorption spectra of the complexes 1 and 2in acetonitrile keeping the concentration ($c = 2 \times 10^{-5}$ M).

Compound	Electronic transition	Composition	Excitation energy (eV)	Oscillator Strength (f)	CI	Assign	λ_{exp} in nm (ϵ in $M^{-1}cm^{-1}$)
1	$S_0 \rightarrow S_4$	H-3→L H-5→L	2.8284 (438 nm) 3.2150 (385 nm)	0.0515 0.0248	0.6800 0.6866	¹ MLCT	405 (26722)
	$S_0 \rightarrow S_{10}$	H→L+1	3.8822 (319 nm)	0.2263	0.5165	¹ ILCT	327 (14725)
	$S_0 \rightarrow S_{25}$	H→L+5	4.6646 (265 nm)	0.1538	0.4619	¹ MLCT/ ¹ LLCT	267 (75764)
	$S_0 \rightarrow S_2$ $S_0 \rightarrow S_3$	H-1→L H-2→L	2.8336 (437 nm) 2.9175 (424 nm)	0.0134 0.0377	0.6594 0.6358	¹ MLCT ¹ MLCT	437(5631)
2	$S_0 \rightarrow S_4$	H→L+1	2.9774 (416 nm)	0.1000	0.6607	¹ ILCT	385 (5429)
	$S_0 \rightarrow S_7$	$H-2 \rightarrow L+1$	3.4143 (363nm)	0.0132	0.6083	¹ MLCT	369 (6268)
	$S_0 \rightarrow S_{10}$	H-5→L	3.6114 (343 nm)	0.1543	0.5641	¹ ILCT	328 (9724)
	$S_0 \rightarrow S_{39}$	H-5→L+2	4.8800 (254 nm)	0.8658	0.4158	¹ ILCT	254 (43477)

 Table 3 Main calculated optical transition for complexes 1, 2 and 3 with vertical excitation

 energies and oscillator strength in acetonitrile.

In order to analyze the nature of absorption, we performed an NTO analysis based on the calculated transition density matrices. This method offers the most compact representation of the transition density between the ground and excited states in terms of an expansion into single-particle transitions (hole and electron states for each given excitation). Here we refer to the unoccupied and occupied NTOs as "electron" and "hole" transition orbitals, respectively. Note that NTOs are not the same as virtual and occupied MO pairs from the ground state calculations. Table 4 illustrate the natural transition orbitals (NTOs) for mononuclear complexes (1 and 2) respectively.

Table 4 Natural transition orbitals (NTOs) for the complexes illustrating the nature of singlet excited states. For each complexes, the respective number of the state, transition energy (eV), and the oscillator strength (in parentheses) are listed.

Complex	Transition	Hole	Electron	Assignment
1	S ₄ W=0.92 2.82 eV (0.05)	000 000		MLCT
	$S_{10} \\ W=0.94 \\ 3.21 eV (0.02)$		CCC CCC	ILCT
	S_{25} W=0.42 4.66 eV (0.15)	soft of		LLCT
2	$S_{2} \\ W=0.86 \\ 2.83 \text{ eV} \\ (0.03)$	A A		MLCT
	$S_{3} = 0.79$ 2.91 eV (0.03)			MLCT
	S ₄ W=0.87 2.97 eV (0.1)			ILCT
	S_7 W=0.72 3.414 eV (0.01)			MLCT
	$S_{10} \\ W=0.62 \\ 3.61 \text{ eV} \\ (0.15)$			ILCT
	$S_{39} \\ W=0.33 \\ 4.88 \text{ eV} \\ (0.86)$		Ş.	ILCT/LLCT

Based on the TDDFT NTO analysis, it is clear that the absorption bands at longer wavelength region of these two complexes are purely metal to ligand charge transfer band. In complex 1 the metal charge density completely shifts over quinoline moiety and in complex 2, metal charge

density is delocalized throughout the anthracene and quinoline moiety in their excited states S_4 and S_2 respectively which in turn makes the metal center devoid of electron density.

The higher energy absorptions of complex **1** comprises of intraligand charge transfer band and less contributing ligand to ligand charge transfer band where electron density moves from fluorine moiety to carbonyl ligands. In case of complex **2**, higher energy absorption bands are observed due to ILCT transition with weaker MLCT character as the four excited states (S_4 , S_7 , S_{10} , S_{39}) depicts that the charge density moves in between two ligand fragments and CO ligands.

The emission spectral behavior of two mononuclear rhenium complexes was recorded in acetonitrile solution at room temperature. The complexes displayed poor luminescence property due to the excited state quenching in presence of $[Re(CO)_3]^+$ core, which practically makes them non-emitters.

3.6. Geometry optimization and electronic structure

Molecular structures of the complexes **1** and **2** were optimized by DFT at their electronic ground state (S₀) using LANL2DZ basis set. The optimized structures of the complexes are given in Table S1. The optimized ground state structures of complexes **1**and**2** at their singlet (S₀) state, possesses distorted octahedral geometry around Re(I) metal center. The *fac*-[Re(CO)₃]⁺ core is consisted with each complexes having the angles of ~90° between the CO ligands. Theoretical structural parameters are in excellent agreement with the experimental data for the complexes for which X-ray data are available. In these complexes all the Re-C bond length occurs near 1.91 Å and Re-N bond length occurs near 2.25 Å. The Re-Cl bond length of all the complexes is slightly longer than the Re-C and Re-N bond lengths. All these values deviate from the experimental factors such as crystal packing and the impact of the medium.





The partial frontier molecular orbital compositions in their singlet ground state (S_0) are listed in Table S2. The partial molecular orbital diagram of frontier molecular orbital, which are mainly involved in the electronic transitions for mononuclear complexes **1** and **2** are shown in Fig. 6.

In the ground state (S_0), the energy difference between HOMO (H) and LUMO (L) of all three mononuclear complexes are very similar to each other, which is 2.91 eV and 2.92 eV for complexes 1 and 2 respectively. Clearly, the energy gap between HOMO and LUMO is is comparable to each other. Each mononuclear rhenium(I) complex possesses ligand consist of two moiety joined through imine bond. HOMO of the complexes shows high electron densities around fluorene [FL (84%)] and anthracene [Anth (90%)] moiety for **1** and **2** respectively but, in case of LUMO, high electron density is observed in other part of the ligands i.e. quionline moiety (in the range of 42- 55%). In these two complexes H-1 lies in the range of 0.21-0.63 eV

below the respective HOMO levels and H-2 resides below H-1 by ~0.10 eV. This calculation indicates that H-1 and H-2 levels of these complexes are almost degenerate. Metal orbital contribution towards molecular orbitals occurs in lower energy levels. Predominant participation of rhenium d orbitals occurs from H-2 energy level where ~45% or more contribution arises due to the metal center. Partial involvement of π^* orbital of CO contributes ~25% whereas the p orbital of Cl contributes ~22% in each complex. The HOMO–3 and HOMO–4 are apart from each other by 0.35 eV in 1, 0.12 eV in 2 and 0.06 eV. LUMO (L) and L+1 of all mononuclear complexes originates from the ligand π^* orbital localized on the C=N bond, quinoline moiety and aromatic systems attached to the C=N bond contribution.

3.7. Anion sensing properties

The complexes 1, 2 and ligands L_1 , L_2 are insoluble in water. We have checked the compatibility of these compounds in water through UV-Vis and luminescence spectroscopy by making a stock solution in DMSO. But, addition of cyanide ion in water medium slowly destroys the system (Fig S16). So, the anion binding properties of these compounds have been studied by spectrophotometric and fluorometric titration method in acetonitrile solution (20µM) at room temperature. Tetrabutylammonium salts of OH⁻, F⁻, Cl⁻, OAc⁻, Br⁻, CN⁻, I⁻ were used in this study. Among all the compounds, only complex 2 responded positively towards cyanide ion. All the other anions (OH⁻, F⁻, Cl⁻, OAc⁻, Br⁻, I⁻) remained silent upon addition of 10 equivalents (Fig. 5) of each anion. The absorption titration curve of 2 with cyanide ion passes through several isobestic points in UV-Vis region. These isobestic points indicate the formation of new species in the solution medium. In the electronic absorption spectrum, the ¹MLCT ($d\pi(\text{Re}) \rightarrow L_2$) absorption band at 435 nm exhibits a red shift to 495 nm with a sharp isobestic point at 467 nm (Fig. 7) when cyanide ion concentration slowly increases. It is clearly visible that the peak at 435 nm gradually decreases with the simultaneous increment of the peak at 495 nm. It is assumed that cyanide ion interacts with the complex by attacking the imine bond and forming a 2-CN adduct (shown in scheme 3). The binding of cyanide ion is expected to enrich the electron density of the nitrogen atom of imine bond attached to the anthracene unit and thus render the ¹MLCT transition to occur at lower energy. A plot of the absorbance ratio at 495 and 435 nm (A_{495}/A_{435}) vs concentration of cyanide clearly indicates that A_{435}/A_{495} increases linearly with R² = 0.95307.



Figure 7. Absorption titration of **2** ($c = 2 \times 10^{-5}$ M) with CN⁻ up to 2.5 equivalent ($c = 2 \times 10^{-3}$ M) in acetonitrile (left); The ratiometric plot of absorbance ratio at 495 and 435 nm vs concentration of cyanide ion (middle); Selective change in absorption in presence of various anions (right).

We have investigated the luminescence properties of the non-emissive complexes 1 and 2 in presence of various anions (OH⁻, F⁻, Cl⁻, OAc⁻, Br⁻, CN⁻, I⁻) in acetonitrile at room temperature. Both the complexes were excited with their corresponding lowest energy absorption band and the spectral change was monitored by varying those anions. An appreciable change was observed for 2 in presence of cyanide ion. The non-emissive complex 2 displayed a strong emission at 505 nm (Excited at 437 nm) when 15 equivalents of cyanide ion was added to the complex solution (Fig. 8). This observation suggests that the upcoming cyanide ion somehow can prevent the conjugation between anthracene and quinoline unit which is likely to be observed in the ground state picture of ligand unit in 2. Therefore, the interruption of conjugation has occurred by the addition of cyanide ion into the imine bond attached with anthracene moiety. As a result, the ICT (intramolecular charge transfer transition) process stopped and the fluorophore moiety becomes free to emit. We have calculated the detection limit on the basis of $3\sigma/k$, where σ is the standard deviation of blank measurement. The calculated detection limit is found to be 7.0×10^{-7} M. LOD (limit of detection) value indicates sensitivity of the probe towards the analyte. The lower the value, the better is the sensitivity. Table S4 contains comparative studies on LOD of some recently published works. Our probe has relatively higher detecting ability over the other works while a very few are better in comparison to the present work. In order to further investigate the binding constant of complex 2 with incoming cyanide ion, a plot of $1/\Delta I$ (where, $\Delta I = I - I_0$, I =intensity after cyanide addition, I_0 = intensity before cyanide addition) vs 1/[CN⁻] is carried out. As a result, the fluorescence binding constant is found to be $4.4 \times 10^{-4} \, \text{M}^{-1}$.



Figure 8. Spectrofluorometric titration of **2** ($c = 2 \times 10^{-5}$ M) with 10 equivalents of TBACN in acetonitrile solution at 437 nm (left). The plot of $1/\Delta I \text{ vs. } 1/[\text{CN}^-]$, where $\Delta I = I - I_0$ (I = intensity after cyanide addition, I_0 = intensity before cyanide addition) (right).

For the better insight of the reaction occurring in presence of CN^{-} ion, ¹H NMR titration was carried out in CD_3CN solution of **2** and the change in spectra was recorded after gradual increment of cyanide ion up to 1.5 equivalents. The ¹H NMR peak of aldimine proton at 10.3 ppm disappeared slowly up to the addition of 1.5 equivalents of cyanide ion. A new peak appeared at 7.3 ppm simultaneously which is assigned as the cyanomethanamine proton. The aromatic protons were shifted towards slightly upfield region. This observation supports the fact that the imine bond of **2** was affected by cyanide ion which induces different electronic atmosphere around the aromatic region and caused the aromatic protons as well as the cyanomethanamine proton to shift towards upfield region. The relevant ¹H NMR titration is shown in Fig. 9.



Figure 9. The ¹H NMR titration of complex 2 in CD_3CN solution in presence of 1.5 equivalents of CN^- ion. Generation of cyanomethanamine proton is shown by (*).



Scheme 3 Probable mechanism for the formation of 2-CN adduct.

Furthermore, the time resolved luminescence spectra also give evidence to understand the decay process and the emissive nature of the 2-CN adduct. Life time data are recorded for 2-CN adduct at room temperature in acetonitrile solution when excited at 437 nm. The emission lifetime (τ), radiative (k_r) and nonradiative (k_{nr}) decay rate constant of 2-CN adduct were collected in Table 2. It shows a bi-exponential decay. Upon addition of CN⁻ ion into the solution of 2 enhances the emission intensity as well as the excited state lifetime due to the formation of 2-CN adduct. This photoluminescence property mainly originates from the triplet state charge transfer transitions, which is confirmed by the treatment of triplet oxygen as no quenching of emission intensity occurs. The short Stokes shift of 2-CN with respect to the longer wavelength absorption of 2 reveals the ligand-centered ³IL nature of the T₁ state of 2-CN.

4. Conclusion

In summary, we have synthesized two Schiff base based ligands (L_1 and L_2) and two monomeric rhenium(I) complexes of these two ligands. The aim of the present work is to explore their optical properties and reactivity with various anions. The complexes are characterized by different spectroscopic techniques and X-ray crystal structure determination. This work includes investigation of the ground and excited-state geometries of both the ligands and complexes as well as the study of absorption and luminescence properties of two rhenium(I) complexes by DFT and TDDFT methods. Furthermore, the complex 2 has shown a very interesting photophysical property by selective binding with cyanide ion in acetonitrile solution. The spectral change of complex 2 in presence of high amount of cyanide is prominent in UV-Vis spectroscopy as well as in fluorescence spectroscopy. Proton NMR spectra confirms that the change in spectral response is due to the attachment of cyanide ion into the imine bond of complex 2. So, the studies presented herein provide valuable information about the synthetic strategy of metal complexes as well the ligands. Further research aimed at the synthesis of mononuclear/polynuclear rhenium(I) complexes with multiple important ligands is currently in progress.

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Highlights

- Reaction of Re(CO)₅Cl with two Schiff base ligands provides two rhenium(I) complexes. •
- Crystal structure of two complexes is determined. •
- Complex 2, having anthracene moiety shows red shift in UV-Vis spectra as well as an increment in emission intensity after addition of cyanide ion.
- The spectral change is attributed to the result of an addition reaction occurring in imine ٠ bond of complex 2.

There is no declaration of interest.

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