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Syntheses, characterizations and theoretical calculations of rhodium(III) 1,2-naphthoquinone-1-oxime complexes

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ABSTRACT

Rhodium(III) complexes of 1,2-naphthoquinone-1-oxime (1-nqo) [Rh(1-nqo)L₂Cl₂] **1–3** [**1**, L = 4-methylpyridine (mpy); **2**, L = 4-phenylpyridine (ppy); **3**, L = 4-acetylpyridine (apy)] were prepared. The structure of complex **1** is analyzed by single crystal X-ray crystallography. All of the complexes were characterized by mass spectrometry, ¹H–¹H COSY NMR and FT-IR. UV–Vis absorption spectroscopy and cyclic voltammetry were employed to investigate the electronic transition behaviors of the complexes. The complexes displayed irreversible metal-localized two-electron reductions from Rh^{III} to Rh¹ on the cyclic voltammogram. While the low-energy absorptions at λ_{max} of 488–490 nm on the UV–Vis spectra of the complexes were related to metal to 1-nqo ligand charge transfer [MLCT, d π (Rh) $\rightarrow \pi^*(1-nqo)$] and chloride to 1-nqo ligand charge transfer [LLCT, p π (Cl) $\rightarrow \pi^*(1-nqo)$] based on the theoretical calculations using time-dependent density functional theory (TD-DFT).

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1. Introduction

1,2-Naphthoquinone-1-oxime which is abbreviated as 1-nqoH is the first organic substance that was found to form precipitates with metal ions [1]. 1-nqo and its isomer, 1,2-naphthoquinone-2-oxime (2-nqo), are good chelating agents for transition metals including ruthenium and rhodium [2–13]. The formed complexes displayed interesting electron transfer properties [4,6,7]. Theoretical calculations for rhodium complexes can be performed by density functional theory (DFT) [14], using mPW1PW91 method with SDD basis set and relativistic effective core potential (ECP) for rhodium [15], as well as B3LYP method with LanL2DZ adding ECP basis set for rhodium [16–18].

As an extension of our studies on 1,2-naphthoquinone-monooxime (nqo) complexes of transition metals, herein we present the syntheses of three dichloride-rhodium(III) 1-nqo complexes containing different pyridine type co-ligands, [Rh(1-nqo)(mpy)₂Cl₂] **1** (mpy = 4-methylpyridine), [Rh(1-nqo)(ppy)₂Cl₂] **2** (ppy = 4-phenylpyridine) and [Rh(1-nqo)(apy)₂Cl₂] **3** (apy = 4-acetylpyridine). The structure of complex **1** is analyzed by single crystal X-ray crystallography. All of the complexes are characterized by mass spectrometry, ¹H–¹H COSY NMR and FT-IR. Theoretical calculations are conducted on the complexes by DFT at B3LYP level, using the basis sets of LanL2DZ adding ECP basis set for Rh and 6-31G for other atoms. The singlet–singlet electronic transitions and the energy level of the triplet orbital ³ π^* of the complexes are calculated by timedependent density functional theory (TD-DFT) methods [19] using B3LYP functional with the same basis set as ground state. The electronic transition and electrochemistry behaviors of the complexes are discussed based on TD-DFT calculations.

2. Experimental

2.1. Materials and equipments

All chemicals were purchased from commercial sources and used as received, including hydrated rhodium(III) chloride (RhCl₃·3H₂O, Johnson Matthey, Materials Technology, UK), 1,2-naphthoquinone-1-oxime (named also as 1-nitroso-2-naphthol, Lancaster synthesis, England), 4-methylpyridine (Sinopharm Chemical Reagent Co., Ltd., China), 4-phenylpyridine (Aldrich Chemical Co., Inc., USA), 4-acetylpyridine (Alkali Metals Ltd., India), tetrabutylammonium hexafluorophosphate (TBAP, Sigma Chemical Company, USA). Preparative thin layer chromatographic (TLC) plates were prepared from silica GF254 (Qingdao Haiyang Chemical Co., Ltd., China).





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Single crystal X-ray diffraction measurement was conducted on a Bruker SMART 1000 CCD diffractometer (Bruker, Germany). Fast atom bombardment mass spectra (FAB MS) were measured on a MAT 95 mass spectrometer (Finnigan, USA). ¹H-¹H COSY NMR spectra were obtained from a DPX-400 NMR spectrometer (Bruker BioSpin, Swiss). Infrared spectra were recorded on a Spectrum One FT-IR Spectrometer (Perkin-Elmer, USA) with samples prepared as KBr pellets. Electronic absorption spectra were recorded on a UV-2100 spectrophotometer (Beijing RayLeigh Analytical Instrument Corp, China). Cyclic voltammetry was conducted using a multichannel electrochemical analyzer VMP3 (Bio-Logic-Science Instruments, France). All electrochemical data was obtained with a glass cell, equipped with a glassy carbon working electrode, a platinum wire reference electrode, and a platinum wire as the auxiliary electrode filled with CH₂Cl₂ containing 0.1 mol dm⁻³ tetrabutylammonium hexafluorophosphate (TBAP) as a supporting electrolyte. The ferrocene/ferrocenium couple was used as an internal standard. All of the reported potentials were relative potentials (calibrated to the ferrocene internal standard $[Fc^{0/+1}]$ as zero potential).

2.2. Preparation of rhodium(III) complexes

The reaction mixture of $RhCl_3 \cdot 3H_2O$ (0.053 g, 0.2 mmol) and 1-nqoH (0.069 g, 0.4 mmol) ($RhCl \cdot 3H_2O$:1-nqoH = 1:2, mol/mol) in 50 ml ethanol was first refluxed for two hours. The corresponding pyridine type ligand (mpy, ppy or apy) of equal molar amount with the 1-nqoH was added to the hot mixture and was refluxed for another 2.5 h. The solvent was then removed under vacuum and the residue was chromatographed by thin layer chromatography (TLC). Orange products were isolated from each reaction mixture respectively as $[Rh(1-nqo)(mpy)_2Cl_2]$ **1**, $[Rh(1-nqo)(ppy)_2Cl_2]$ **2** and $[Rh(1-nqo)(apy)_2Cl_2]$ **3** by using solvent mixture of *n*-hexane/ CH_2Cl_2 (v/v of 1:7, 1:5 and 1:5, respectively) as eluant.

2.3. X-ray crystallography

Single crystals of **1** were obtained by slow diffusion of *n*-hexane into dichloromethane solution of the complex. A red single crystal with approximate dimensions of $0.10 \times 0.20 \times 0.37 \text{ mm}^3$ was selected and sealed in a glass capillary. All measurements and data was made and recorded on a Bruker SMART 1000 CCD diffractometer equipped with a graphite monochromated Mo K α radiation (λ = 0.071073 nm). The data were collected at room temperature (301 ± 1 K). Crystallographic data and experimental details for complex **1** were summarized in Table 1. A total of 15136 reflections were collected, of which 4917 were independent ($R_{int} = 0.028$) and 3784 observed reflections with $I > 2\sigma(I)$ were used in the structure analysis. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms could be found from the difference Fourier map but were placed at geometrical sites with C–H = 0.95 Å.

2.4. Theoretical calculations

Full geometry optimizations were performed at an Intel Pentium IV 3.0 G computer employing the GAUSSIAN 03 software package suite of programs, using experimental geometry as input for complex **1** [20]. The complexes **1–3** were treated as an open-shell system using the spin unrestricted DFT wavefunction, i.e. the Becke three-parameters exchange functional in combination with the LYP correlation functional of Lee, Yang and Parr, B3LYP [21,22], with 6-31G basis set for C, H, O, N, and Cl atoms, and relativistic effective core potential basis set of double zeta quality Hay and Wadt Los Alamos ECP [23] basis set LanL2DZ for Rh atom. All geometry optimizations were performed without any symmetry

Table 1

Crystallographic data and experimental details for [Rh(1-nqo)(mpy)₂Cl₂] 1.

| Compound | $[Rh(1-nqo)(mpy)_2Cl_2]$ 1 |
|---|---|
| Empirical formula | RhO ₂ N ₃ C ₂₂ H ₂₀ Cl ₂ |
| Formula weight | 532.23 |
| Crystal color, habit | red, block |
| Crystal dimensions (mm) | $0.10 \times 0.20 \times 0.37$ |
| Crystal system | monoclinic |
| Lattice type | Primitive |
| Space group | $P2_1/n$ (no. 14) |
| a (Å) | 14.691(2) |
| b (Å) | 9.252(1) |
| <i>c</i> (Å) | 17.469(3) |
| α (°) | 90 |
| β(°) | 111.632(2) |
| γ (°) | 90 |
| $V(Å^3)$ | 2207.1(6) |
| Ζ | 4 |
| D_{calc} (g/cm ³) | 1.602 |
| F(0 0 0) | 1072 |
| Total number of reflections measured | 15136 |
| Number of symmetry-independent reflections | 4917 |
| Number of reflections > 2σ threshold | 3784 |
| $R^{\rm a}$ and $R_{\rm w}^{\rm b}$ [I > $2\sigma(I)$] | 0.035 and 0.037 |
| maximum and minimum peaks $(e^{-} Å^{-3})$ | 1.21 and -0.36 |

^a $R = ||F_o| - |F_c||/|F_o|$.

^b $R_{\rm w} = [w (|F_o| - |F_c|)^2 / w F_o^2]^{1/2}.$

constrains and the convergence accuracy were calculated using the default procedures. After frequency calculations are performed on all of the structure optimized complexes, the optimized stationary points of complexes **1–3** are confirmed to be local minima as no imaginary vibrational frequencies appear. The contour plots of molecular orbitals (MOs) were plotted using the GAUSSION 03 view program.

Based on the optimized geometries, the vertical excitation energies of both the singlet and triplet excited states of the complexes were calculated at TD-B3LYP theoretical level.

3. Results and discussion

3.1. Crystal structure of complex 1

In order to establish the molecular structure of the complex, single crystal X-ray diffraction analysis was carried out for single crystal of 1. The corresponding molecular structure is shown in Fig. 1. Selected bond distances and angles are summarized in Table 2. The central Rh(III) adopts a pseudo-octahedral geometry. The two nitrogen atoms, N(2) and N(3) of the mpy ligands locate in the equatorial plane with a *cis*-configuration. The other two positions of the same equatorial plane are bridged by the oximato N and quinonal O [N(1)] and O(1)] of the 1-ngo ligand. The bidentate 1-ngo is almost co-planar with the metal equatorial plane with the dihedral angle of 5.48(7)°. The dihedral angle of the metal equatorial plane with the two methyl pyridine ligands is 126.8(1)° and 44.5(1)°, respectively. The remaining two vacant sites are occupied by two chlorides. The two chloride ions are at the apical trans-positions which are nearly perpendicular to the equatorial plane with the bond angle of [Cl(2)-Rh(1)-Cl(1) 176.83(4)°]. The bidentate 1ngo ligand coordinates to the Rh(III) center through its oximato N and guinonal O atoms to form a stable five-membered metalchelate ring which helps this geometry to gain an extra stability. This coordination mode is commonly observed in other Rh(III) complexes containing 1-nqo and its isomer 2-nqo as ligands [6,24].

3.2. Synthesis and characterization of rhodium(III) complexes

Three orange complexes, **1–3**, were prepared by reflux the corresponding pyridine type ligand, mpy, ppy or apy with the reaction



Fig. 1. Molecular structure of [Rh(1-nqo)(mpy)₂Cl₂] 1.

Table 2 Selected bond lengths (Å) and angles (°) for [Rh(1-nqo)(mpy)₂Cl₂] 1 together with the calculated values by DFT

| , , , , , , , , , , , , , , , , , , , | | |
|---------------------------------------|--------------------|------------------|
| | Experimental value | Calculated value |
| Rh(1)-Cl(1) | 2.329(1) | 2.4541 |
| Rh(1)-Cl(2) | 2.342(1) | 2.4561 |
| Rh(1)-N(1) | 1.979(3) | 2.0295 |
| Rh(1)-N(2) | 2.053(3) | 2.0825 |
| Rh(1)-N(3) | 2.085(3) | 2.1108 |
| Rh(1)–O(1) | 2.025(2) | 2.0539 |
| C(1)-O(1) | 1.279(5) | 1.3090 |
| N(1)-O(2) | 1.242(4) | 1.2733 |
| Cl(2)-Rh(1)-Cl(1) | 176.83(4) | 178.17 |
| O(1)-Rh(1)-Cl(1) | 88.57(9) | 90.27 |
| N(1)-Rh(1)-Cl(1) | 89.8(1) | 89.11 |
| | | |

90.84

90.06

88.32

89 51

90 50

91.14

91.7(1)

90.3(1)

88.55(9)

88.5(1)

91.1(1)

91.1(1)

N(2)-Rh(1)-Cl(1)

N(3)-Rh(1)-Cl(1)

O(1)-Rh(1)-Cl(2)

N(1)-Rh(1)-Cl(2)

N(2)-Rh(1)-Cl(2)

N(3)-Rh(1)-Cl(2)

mixture of RhCl₃·3H₂O and 1-nqoH in ethanol (Scheme 1). The complexes are characterized by mass spectroscopy, $^{1}H^{-1}H$ COSY NMR and FT-IR after TLC purification (Table 3).

Intense peak for $[M-CI]^+$ at m/z 496 is observed on the FAB MS spectrum of complex **1** as the largest daughter ion with no molecular ion peak present. Similar FAB MS spectra are also observed for complexes **2** and **3**. The observed common $[M-CI]^+$ pattern indicates that there are also one 1-nqo ligand, two pyridine type ligands and two chlorides coordinated to the Rh center for **2** and **3** as suggested by the molecular structure of **1** that obtained by X-ray crystallography. On the basis of ¹H-¹H COSY NMR measurements, the ¹H NMR signals assignments are conducted for all of the complexes (Table 3). Typical ¹H-¹H COSY NMR spectrum of complex **1** is shown in Fig. 2. On all of the spectra, the integral ratio of ¹H signals for 1-nqo and pyridine type ligands is 1:2, which is consistent with FAB MS results. Complexes **1–3** give very similar patterns in the ¹H NMR spectra for the coordinated 1-nqo and pyridine type ligands, showing that the chemical environments



Scheme 1. Reaction of RhCl-3H₂O with 1-nqoH followed by treatment with the pyridine type ligand.

| Table 3 |
|---------|
|---------|

FAB MS, IR and ¹H NMR data of complexes 1–3.

| Complex | FAB $MS^*(m/z)$ | IR spectra (cm ⁻¹) | ¹ H NMR spectra (1D) (δ (ppm), J (Hz)) |
|---|-----------------|--|--|
| [Rh(1-nqo)(mpy) ₂ Cl ₂] 1 | 496 (532) | $\begin{array}{l} \delta_{asC-H} = 1432 \\ \delta_{sC-H} = 1361 \\ \nu_{N-O} = 1040 \end{array}$ | 9.13 (d, 1H, J = 8.3, H ¹), 8.66 (br.d, 2H, J = 6.5, H ⁷), 8.57 (br.d, 2H, J = 6.4, H ⁷), 7.76 (d, 1H, J = 9.6, H ⁵), 7.66 (m, 2H, H ^{2.4}), 7.48 (m, 1H, H ³), 7.30 (d, 2H, H ⁸), 7.22 (d, 2H, H ^{8'}), 7.19 (s, 1H, H ⁶), 2.48 (s, 3H, H ⁹ or H ^{9'}) |
| [Rh(1-nqo)(ppy) ₂ Cl ₂] 2 | 620 (656) | $v_{\rm N-O}$ = 1072 $\delta_{\rm C-H}$ = 765, 730, 693 | 9.21 (d, 1H, $J = 8.2$, H ¹), 8.98 (br.d, 2H, $J = 6.7$, H ⁷), 8.90 (br.d, 2H, $J = 6.8$, H ⁷), 7.72 (d, 1H, J = 9.4, H ⁵), 7.68 (m, 2H, H ⁸), 7.72–7.66 (m, 4H, phenyl), 7.65–7.61 (m, 4H, H ^{2.4.8'}), 7.57–7.52 (m, 6H, phenyl), 7.46 (m, 1H, H ³), 7.30 (d, 1H, J = 9.4, H ⁶) |
| [Rh(1-nqo)(apy) ₂ Cl ₂] 3 | 552 (588) | $v_{C=0} = 1697$ $v_{N-0} = 1059$ | 9.13 (m, 1H, H ¹), 9.13 (br.d, 2H, $J = 6.7$, H ⁷), 9.06 (br.d, 2H, $J = 6.6$, H ⁷), 7.91 (dd, 2H, $J = 5.2$, 1.5, H ⁸), 7.84 (dd, 2H, $J = 5.4$, 1.4, H ^{8'}), 7.74 (d, 1H, J = 9.4, H ⁵), 7.67 (m, 1H, H ²), 7.64 (m, 1H, H ⁴), 7.48 (m, 1H, H ³), 7.25 (m, 1H, H ⁶), 2.71(s, 3H, H ⁹ or H ^{9'}), 2.70 (s, 3H, H ⁹ or H ^{9'}) |

Only [M-Cl]⁺ is observed.



Fig. 2. ¹H–¹H COSY NMR spectrum of [Rh(1-nqo)(mpy)₂Cl₂] 1.

of these ligands are very similar. It shows that the ligand spatial arrangement of ${\bf 2}$ and ${\bf 3}$ should be very similar to that of complex ${\bf 1}$.

Infrared spectra of **1–3** show strong bands at 1608–1631, 1513– 1515 and 1435–1437 cm⁻¹ respectively which corresponds to the vibrations of aromatic skeleton [25]. The sharp peaks at 1592– 1593 and 1553–1554 cm⁻¹ are attributed to the pyridine type ligands. The in-plane bending vibrations of methyl group in complex **1** are observed at 1432 cm⁻¹ for δ_{asC-H} and 1361 cm⁻¹ for δ_{sC-H} . For complex **2**, the characteristic vibrations for mono-substituted phenyl ring are found at 765, 730 and 693 cm⁻¹. While the vibration of carbonyl group on the pyridine type ligand of complex **3** appears at 1697 cm⁻¹.

3.3. Electron transfer characterization

The UV–Vis absorption spectra of the Rh(III) complexes and 1-nqoH in CH_2Cl_2 are depicted in Fig. 3, while the spectral data are summarized in Table 4. In UV–Vis absorption spectra, there is a strong absorption in the UV region (270–290 nm) and three absorptions (402–410 nm, 488–490 nm and shoulder peaks of 524–528 nm) in the visible region for complexes **1–3**. All of absorption peaks for the complexes have been assigned based on TD-DFT theoretical calculations (see Section 3.5).

Electrochemical properties of **1–3** are studied by cyclic voltammetry in dichloromethane containing 0.1 mol dm⁻³ TBAP.



Fig. 3. UV-Vis absorption spectra of 1-nqoH (solid line), complexes 1 (dash line), 2 (dot line) and 3 (dash dot line) in CH₂Cl₂.

Table 4

Calculated excited states, singlet excitation energies (*E* (ev)), absorption bands, oscillator strengths (*f*), transition configuration and coefficient by TD-DFT and experimental UV– Vis absorption bands of complexes **1–3** together with those of 1-nqoH.

| Compound | Excited state | <i>E</i> (ev) | $\lambda_{calc} (nm)$ | f | Transition configuration [*] (CI coefficient) | | $\lambda_{ m exp} ({ m nm}) (\epsilon ({ m 10^4 L mol^{-1} cm^{-1}})$ |
|--|---------------|---------------|-----------------------|--------|--|--------------|--|
| 1-nqoH | | | | | | | 374 (0.73) |
| | | | | | | | 274 (1.81) |
| $[Rh(1-nqo)(mpy)_2Cl_2]$ 1 | | | | | | | 528 sh (0.18) |
| | 1 | 2.57 | 483 | 0.003 | HOMO-1 \rightarrow LUMO | -0.40 (32 %) | 490 (0.31) |
| | | | | | $HOMO \rightarrow LUMO$ | 0.51 (53 %) | |
| | 5 | 3.1 | 401 | 0.0349 | $HOMO-1 \rightarrow LUMO$ | 0.39 (31 %) | 402 (1.06) |
| | | | | | $HOMO \rightarrow LUMO$ | 0.34 (23 %) | |
| | 22 | 4.35 | 285 | 0.0079 | $HOMO-4 \rightarrow LUMO + 1$ | -0.36 (25 %) | 290 (1.77) |
| | | | | | $HOMO-4 \rightarrow LUMO + 2$ | 0.53 (55 %) | |
| [Rh(1-nqo)(ppy) ₂ Cl ₂] 2 | 1 | 2.43 | 510 | 0.0001 | HOMO-1 \rightarrow LUMO + 1 | -0.32 (20 %) | 524 sh (0.17) |
| | | | | | $HOMO \rightarrow LUMO + 1$ | 0.41 (34 %) | |
| | 2 | 2.45 | 505 | 0.0003 | $HOMO-4 \rightarrow LUMO$ | 0.46 (42 %) | |
| | 3 | 2.58 | 480 | 0.0039 | $HOMO-1 \rightarrow LUMO$ | -0.47 (44 %) | 488 (0.21) |
| | | | | | $HOMO \rightarrow LUMO$ | 0.48 (46 %) | |
| | 6 | 2.96 | 419 | 0.0313 | $HOMO-1 \rightarrow LUMO$ | 0.44 (38 %) | 410 (0.63) |
| | | | | | $HOMO \rightarrow LUMO$ | 0.36 (26 %) | |
| | 50 | 4.62 | 268 | 0.3197 | HOMO-8 \rightarrow LUMO + 2 | 0.41 (34 %) | 270 (2.94) |
| [Rh(1-nqo)(apy) ₂ Cl ₂] 3 | 1 | 2.44 | 508 | 0.0001 | HOMO-1 \rightarrow LUMO + 3 | 0.41 (34 %) | 524 sh (0.22) |
| | | | | | $HOMO \rightarrow LUMO + 3$ | 0.45 (41 %) | |
| | 2 | 2.48 | 499 | 0.0004 | $HOMO-4 \rightarrow LUMO$ | 0.53 (57 %) | |
| | 3 | 2.61 | 476 | 0.0038 | $HOMO-1 \rightarrow LUMO$ | 0.43 (37 %) | 488 (0.32) |
| | | | | | $HOMO \rightarrow LUMO$ | 0.48 (47 %) | |
| | 12 | 3.11 | 398 | 0.0135 | $HOMO-2 \rightarrow LUMO + 2$ | 0.55 (60 %) | 410(0.98) |
| | | | | | HOMO-1 \rightarrow LUMO + 2 | 0.35 (25 %) | |
| | 41 | 4.16 | 298 | 0.0662 | HOMO-8 \rightarrow LUMO + 2 | 0.45 (41 %) | 290(1.95) |
| | | | | | HOMO-7 \rightarrow LUMO + 2 | 0.47 (45 %) | |

The absolute value of the transition coefficient for transition is above 0.3 that has been listed in front of parentheses.

Representative cyclic voltammogram of complex **3** is shown in Fig. 4. The electrochemical behaviors of the complexes resemble that of other dichloride–rhodium(III) complexes containing the isomer of 1-nqo, 2-nqo ligands, such as $[Rh(2-nqo)L_2Cl_2]$ and $[Rh(2-nqo)_2LCl]$ (L = phenylphosphonate or pyridine type ligands) [6]. The cyclic voltammograms of complexes **1–3** show an irreversible, metal-localized two-electron redox pair. The reductive and oxidative peak potentials, E_{red} and E_{ox} , are presented in Table 5. The reductive peak potentials E_{red} are positive-shifted from complex **1** to **2** and further **3**, due to the decrease in π electron-donating ability of the pyridine type ligands in the complexes from mpy to ppy and apy.

3.4. Ground state geometry optimization

Open-shell system spin unrestricted DFT calculations are carried out for complex **1** using experimental geometry as input by wave function B3LYP, with relativistic effective core potential basis set LanL2DZ for Rh atom and 6-31G basis set for C, H, O, N and Cl atoms. Selected calculated bond lengths and angles are listed in Table 2 together with the available experimental data for comparison. Structural optimizations are conducted for complexes **2** and **3**, similarly based on the geometry structure of complex **1**.



Fig. 4. Cyclic voltammogram of [Rh(1-nqo)(apy)₂Cl₂] 3 in CH₂Cl₂ containing 0.1 mol dm⁻³ TBAP; glassy carbon working electrode, scan rate, 100 mV s⁻¹.

Table 5

Electrochemical data for complexes 1-3*.

| | $E_{\rm red}$ (V) vs. Fc ^{0/+1} | $E_{\rm ox}$ (V) vs. Fc ^{0/+1} |
|---|--|---|
| [Rh(1-nqo)(mpy) ₂ Cl ₂] 1 | -1.458 | 0.566 |
| [Rh(1-nqo)(ppy) ₂ Cl ₂] 2 | -1.290 | 0.610 |
| [Rh(1-nqo)(apy) ₂ Cl ₂] 3 | -1.215 | 0.704 |

 $^{*}\,$ All peak potentials are obtained from cyclic voltammetry at 100 mV s $^{-1}$ in CH_2Cl_/ 0.1 mol dm $^{-3}$ TBAP.

3.5. Excited state calculation

UV–Vis spectra reflect the electronic transition behavior of molecules, however usually only the singlet–singlet electronic transitions are easy to be observed as the banned singlet–triplet transitions have a very low absorption coefficient. Singlet–singlet electronic transitions of complexes **1–3** are calculated by TD-DFT method based on the optimized molecular structures. Fig. 5 depicts the plots of the corresponding highest occupied molecular orbital HOMO^s, together with the other two frontier orbitals HOMO^s-1 and HOMO^s-2 for the three complexes. The lowest-unoccupied molecular orbital LUMO^s is also listed in Fig. 5. The compositions of the orbitals are in Table 6. The calculated excited states, singlet excitation energies (*E*/ev), absorption bands, oscillator strengths (*f*), transition configuration and coefficient are in Table 4 together with the experimental UV–Vis absorption bands of complexes **1–3**.

Based on TD-DFT calculations, the intense high-energy absorptions at λ_{max} of 270–290 nm on the UV–Vis spectra can be attributed to LLCT [π (1-nqo) $\rightarrow \pi^*$ (mpy) for complex **1**, $p\pi$ (Cl) $\rightarrow \pi^*$ (ppy) for



Fig. 5. Contour diagrams of the calculated HOMO^s-2, HOMO^s-1, HOMO^s and LUMO^s of complexes 1 (a), 2 (b) and 3 (c).

 Table 6

 Compositions of the frontier molecular orbitals HOMO^s-2, HOMO^s-1, HOMO^s, and LUMO^s for complexes 1–3.

| Complex | Composition (%) | | | | | | | | | | | | | |
|-------------|--|-------|-------|-------|-------|-------|-------|------|------|-------------|-----------------|-----------------|------|------|
| | Molecular obital | Rh | Cl(1) | Cl(2) | 0(1) | O(2) | N(1) | N(2) | N(3) | C_{1-nqo} | C _{L1} | C _{L2} | O(3) | 0(4) |
| [Rh(1-nqo)(| $mpy)_2Cl_2$] 1 | | | | | | | | | | | | | |
| | LUMO ^s | 5.30 | 1.22 | 1.04 | 8.30 | 20.55 | 25.62 | 0.12 | 0.20 | 35.21 | 0.56 | 1.06 | | |
| | HOMO ^s | 22.52 | 7.83 | 7.64 | 12.84 | 9.98 | 2.64 | 0.08 | 0.06 | 34.68 | 0.92 | 0.46 | | |
| | HOMO ^s -1 | 20.42 | 30.14 | 27.32 | 2.1 | 3.85 | 1.17 | 0.01 | 0.2 | 6.63 | 0.63 | 0.58 | | |
| | HOMO ^s -2 | 28.79 | 30.87 | 27.59 | 1.44 | 1.02 | 0.15 | 0.17 | 0.09 | 7.97 | 0.97 | 0.57 | | |
| [Rh(1-nqo)(| ppy) ₂ Cl ₂] 2 | | | | | | | | | | | | | |
| | LUMO ^s | 4.85 | 1.10 | 0.89 | 8.83 | 20.55 | 25.31 | 0.08 | 0.16 | 36.22 | 0.50 | 1.08 | | |
| | HOMO ^s | 15.24 | 3.51 | 3.01 | 16.22 | 13.92 | 3.58 | 0.07 | 0.05 | 42.93 | 0.86 | 0.40 | | |
| | HOMO ^s -1 | 21.29 | 34.32 | 31.57 | 1.02 | 2.85 | 0.72 | 0.11 | 0.21 | 5.66 | 1.03 | 0.73 | | |
| | HOMO ^s -2 | 28.06 | 30.51 | 32.10 | 0.04 | 0.67 | 0.15 | 0.15 | 0.22 | 5.71 | 1.04 | 1.00 | | |
| [Rh(1-nqo)(| apy) ₂ Cl ₂] 3 | | | | | | | | | | | | | |
| | LUMO ^s | 3.14 | 1.16 | 1.00 | 6.48 | 15.80 | 19.20 | 0.95 | 3.75 | 26.96 | 3.51 | 12.39 | 0.91 | 3.45 |
| | HOMO ^s | 12.40 | 2.39 | 2.19 | 16.51 | 14.92 | 3.96 | 0.07 | 0.04 | 46.24 | 0.69 | 0.33 | 0.02 | 0.01 |
| | HOMO ^s -1 | 22.33 | 31.50 | 32.77 | 0.38 | 2.54 | 0.60 | 0.19 | 0.21 | 7.11 | 1.19 | 0.68 | 0.01 | 0.01 |
| | HOMO ^s -2 | 27.14 | 27.21 | 33.46 | 0.17 | 0.54 | 0.18 | 0.13 | 0.30 | 8.65 | 0.82 | 1.01 | 0.02 | 0.02 |

| - | | - |
|----|-----|---|
| Ta | ble | 7 |

Energies of LUMO^t and electrochemical properties for complexes 1-3.

| | [Rh(1- | [Rh(1- | [Rh(1- |
|--------------------------|---|---|---|
| | nqo)(mpy) ₂ Cl ₂] 1 | nqo)(ppy) ₂ Cl ₂] 2 | nqo)(apy) ₂ Cl ₂] 3 |
| E _{LUMO} (a.u.) | -0.04559 | -0.06975 | -0.1022 |
| E _{red} (V) | -1.458 | -1.290 | -1.215 |

complex **2**, and $p\pi(Cl) \rightarrow \pi^*(apy)$ for complex **3**]. The bands at λ_{max} of 402–410 nm are assigned to LLCT $[p\pi(Cl) \rightarrow \pi^*(1-nqo)]$ and MLCT $[d\pi(Rh) \rightarrow \pi^*(1-nqo)]$ for complexes **1–2**, but LLCT $[p\pi(Cl) \rightarrow \pi^*(apy)]$ for complex **3**. The low-energy absorptions at λ_{max} of 488-490 nm are related to metal and chloride to 1-nqo ligand charge transfer excitation [MLCT, $d\pi(Rh) \rightarrow \pi^*(1-nqo)$; LLCT, $p\pi(Cl) \rightarrow \pi^*(1-nqo)$], while the shoulder peaks of 524–528 nm can be attributed to 1-nqo to metal and chloride ligand charge transfer [LMCT, $\pi(1-nqo) \rightarrow d\pi^*(Rh)$; LLCT, $\pi(1-nqo) \rightarrow p\pi^*(Cl)$].

As the energy of the triplet anti-bonding orbital ${}^{3}\pi^{*}$ is lower than that of its singlet counterpart ${}^{1}\pi^{*}$, electrochemical reduction usually occurs as the acceptance of electrons by ${}^{3}\pi^{*}$. Triplet TD-DFT calculations for complexes **1**–**3** are conducted based on the optimized structure. The energies of the corresponding lowestunoccupied molecular orbitals (LUMO^t), E_{LUMO}^{t} are summarized in Table 7 together with the reductive potentials of the complexes, E_{red} . From Table 7, the *p*-substitutions of the pyridine type ligands have effect on the energy of the triplet orbital. The energy decreases along with the decrease of the electron-donating ability of the pyridine type ligand, resulting in higher tendency to accept electrons. This is in agreement with the experimental result of electrochemistry study (E_{red}).

4. Conclusions

In this work, dichloride–rhodium(III) complexes of 1,2-naphthoquinone-1-oxime (1-nqo) containing pyridine type ligands have been synthesized and characterized by single crystal X-ray diffraction analysis, FAB MS, ${}^{1}H{-}^{1}H$ COSY NMR and FT-IR. The 1nqo ligand coordinated to the Rh center as a bidentate ligand through its oxime N and quinone O atoms, based on single crystal X-ray diffraction analysis of [Rh(1-nqo)(mpy)₂Cl₂] **1**. DFT calculations have been carried out for complex **1** by wave function B3LYP with relativistic effective core potential basis set of LanL2DZ for Rh and 6-31G basis set for C, H, O, N, Cl atoms. Structure optimizations have been conducted similarly for the other two complexes. The singlet–singlet electronic transitions and the energy level of the triplet orbital ${}^{3}\pi^{*}$ of the complexes have been calculated by time-dependent density functional theory (TD-DFT) method based on this. The low-energy absorptions at λ_{max} of 488–490 nm on the UV–Vis spectra of the complexes can be mainly assigned to metal to 1-nqo ligand charge transfer [MLCT, $d\pi(Rh) \rightarrow \pi^{*}(1-nqo)$] together with LLCT from chloride atoms to 1-nqo ligand [$p\pi(Cl) \rightarrow \pi^{*}(1-nqo)$]. Based on triplet TD-DFT calculations, the energy of the lowest-unoccupied molecular orbital LUMO^t decreases along with the decrease of electron-donating ability of pyridine type ligand, resulting in higher reductive potential (E_{red}) of the complexes.

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Appendix A. Supplementary material

CCDC 735086 contains the supplementary crystallographic data for complex $[Rh(1-nqo)(mpy)_2Cl_2]$ **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.12.033.

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