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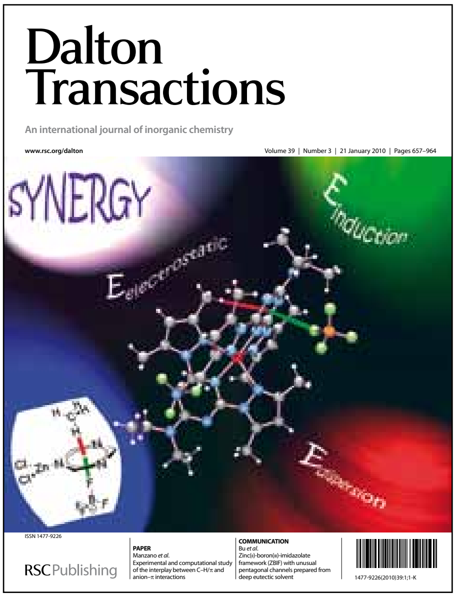

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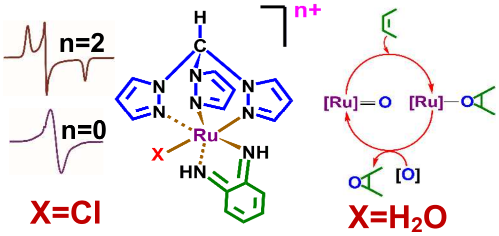
TOC

Redox series including $\{Ru^{II}(bqdi^0)Cl/H_2O\}^{n+}$, $\{Ru^{III}(bqdi^0)Cl\}^{2+}$, $\{Ru^{II}(bqdi^{\bullet-})Cl\}^0$, $\{Ru^{III}(bqdi^0)OH\}^{2+}$, $\{Ru^{IV}(bqdi^0)O\}^{2+}$ and the application of the aqua complex for selective epoxidation process are reported.



Electronic structure and catalytic aspects of [Ru(tpm)(bqdi)(Cl/H_2O)]^n, tpm = tris(1-pyrazolyl)methane and bqdi = *o*-benzoquinonediimine

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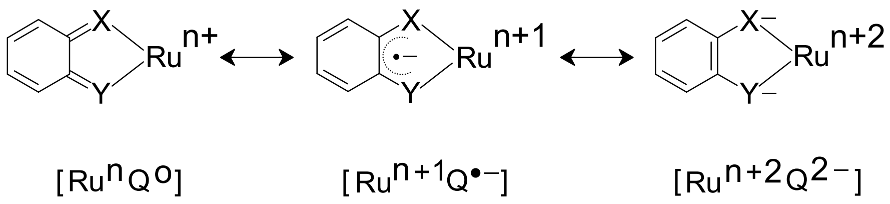
Abstract

The diamagnetic complexes [Ru(tpm)(bqdi)(Cl)]ClO$_4$ ([**1**]ClO$_4$) (tpm = tris(1-pyrazolyl)methane, bqdi = *o*-benzoquinonediimine) and [Ru(tpm)(bqdi)(H$_2$O)](ClO$_4$)$_2$ ([**2**](ClO$_4$)$_2$) have been synthesized. The valence state-sensitive bond distances of coordinated bqdi [C-N: 1.311(5)/1.322(5) Å in [**1**]ClO$_4$; 1.316(7)/1.314(7) Å in molecule **A** and 1.315(6)/1.299(7) Å in molecule **B** of [**2**](ClO$_4$)$_2$] imply its fully oxidised quinonediimine (bqdi^0) character. DFT calculations of **1**$^+$ confirm the {Ru^{II}-bqdi^0} versus the antiferromagnetically coupled {Ru^{III}-bqdi$^{\bullet-}$} alternative. The ^{1}H NMR spectra of [**1**]ClO$_4$ in different solvents show variations in chemical shift positions of the NH (bqdi) and CH(tpm) proton resonances due to their different degrees of acidity in different solvents. In CH$_3$CN/0.1 mol dm^{-3} Et$_4$NClO$_4$, [**1**]ClO$_4$ undergoes one reversible Ru^{II}⇌Ru^{III} oxidation and two reductions, the reversible first electron uptake being bqdi based (bqdi^0/bqdi$^{\bullet-}$). The electrogenerated paramagnetic species {Ru^{III}-bqdi^0}(**1**$^{2+}$) and {Ru^{II}-Q$^{\bullet-}$}(**1**) exhibit Ru^{III}-type (**1**$^{2+}$: $<g>=2.211/\Delta g=0.580$) and radical-type (**1**: $g=1.988$) EPR signals, respectively, as is confirmed by calculated spin densities (Ru: 0.767 in **1**$^{2+}$, bqdi: 0.857 in **1**). The aqua complex [**2**](ClO$_4$)$_2$ exhibits two one-electron oxidations at pH = 7, suggesting the formation of {Ru^{IV}=O} species. The electronic spectral features of **1**^{n} (n = charge associated with the different redox states of the chloro complex: 2+, 1+, 0) in CH$_3$CN and of **2**$^{2+}$ in H$_2$O have been interpreted based on the TD-DFT calculations. The application potential of the aqua complex **2**$^{2+}$ as a pre-catalyst towards the epoxidation of olefins has been explored in the presence of the sacrificial oxidant PhI(OAc)$_2$ in CH$_2$Cl$_2$ at 298 K, showing the desired selectivity with a wide variety of alkenes. DFT calculations based on styrene as the model substrate predict that the epoxidation reaction proceeds through a concerted transition state pathway.

Introduction

The well recognized mixing of ruthenium dπ orbitals and the π orbitals of redox non-innocent quinonoid moieties introduces several manifestations with respect to the valence distribution at the metal-quinonoid interface, as depicted in Scheme 1.[1]



X = Y = NH

X = Y = O

X = O, Y = NH

X = O, Y = NR (R = alkyl, aryl)

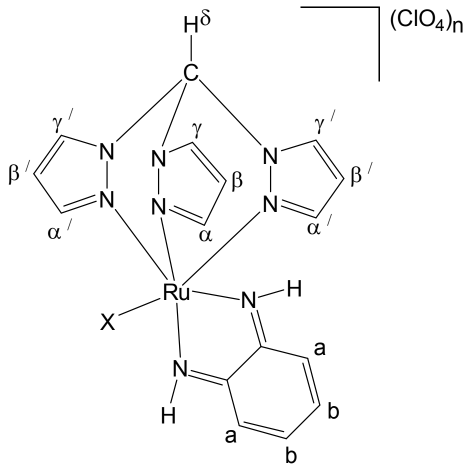
X = S, Y = NH

Scheme 1. Alternative valence configurations of the ruthenium-*o*-quinonoid moiety.

This makes the electronic structure of such complexes sensitive to the molecular frameworks, and in many occasions the experimental results fit well with an intermediate description i.e. the superposition of more than one forms of Scheme 1 instead of any single specific form.[2] Thus, a wide variety of mononuclear[3] and polynuclear[4] ruthenium-quinone complexes have been designed over the past years in combination with co-ligands having different electronic properties. The primary impetus was to develop a fundamental understanding of the bonding and electronic features, however, the catalytic potential of ruthenium-quinonoid complexes including the water oxidation process has also been demonstrated recently.[5]

In this regard the electronic structure aspects of mononuclear ruthenium complexes of *o*-benzoquinonediimine (bqdi) (X=Y=NH, Scheme 1) have been studied in combination with different co-ligands such as π-accepting 2,2/-bipyridine (bpy),[6] 2,2/:6/,2//-terpyridine (trpy),[7a-d] 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz),[7e] 1,4,7-trithiacyclononane ([9]aneS$_3$),[8] 1,4,7,10-tetrathiacyclododecane ([12]aneS$_4$),[9] 1,4,8,11-tetrazacyclotetradecane (cyclam),[10] *p*-cymene (*p*-cym),[11] hexamethylbenzene (hmb),[11] PPh$_3$,[12] CO,[12,13] as well as donating acetylacetonate (acac$^-$),[14] NH$_3$,[6a,f,g,14b,15] and Cl$^-$.[6c,e,7a,12a,14a,b,15b,16] The detailed experimental and theoretical investigations with such varying molecular frameworks revealed an appreciable contribution of the co-ligands in tuning the valence distribution process, including the degree of covalency of the metal-quinone moiety.

The present article deals with the structurally characterised new class of ruthenium-bqdi complexes, [Ru^{II}(tpm)(bqdi)(Cl)]ClO$_4$ ([**1**]ClO$_4$) and [Ru^{II}(tpm)(bqdi)(H$_2$O)](ClO$_4$)$_2$ ([**2**](ClO$_4$)$_2$), **(*CAUTION!* Perchlorate salts of metal complexes are generally explosive. Care must be taken while handling such complexes)**, incorporating the facially coordinating scorpionate[17] co-ligand, tris(1-pyrazolyl)methane (tpm) (Scheme 2). The electronic structural features in accessible redox states of $\mathbf{1}^n$, n = 2+, 1+, 0, have been scrutinised *via* experimental and theoretical analyses.



X = Cl, n = 1: [**1**]ClO_4

X = H_2O, n = 2: [**2**]$(ClO_4)_2$

Scheme 2. Representation of complexes [**1**]ClO_4 and [**2**]$(ClO_4)_2$ along with atom labelling.

Furthermore, the potential application of the corresponding aqua-derivative (**2**$^{2+}$) as a pre-catalyst towards the catalytic epoxidation of alkenes has been explored. While the traditional method for epoxidation of alkenes involves the use of organic peracids with the disadvantages of (i) the formation of organic waste, (ii) a narrow substrate scope, and (iii) the inconvenience in separating the products,[18] other, better oxidants have been employed as efficient and convenient reagents.[19] For instance, ruthenium-complex catalysed epoxidation of olefins using TBHP (*tert*-butylhydroperoxide) as oxidant was first reported by Nishiyama *et al.* in 1997.[20] Consequently, a variety of ruthenium complexes have been successfully utilised for epoxidation reactions in the presence of such suitable oxidants.[20,21]

Results and discussion

Synthesis and characterisation

The chloro complex $[Ru^{II}(tpm)(bqdi)(Cl)]ClO_4$ ($[\mathbf{1}]ClO_4$) (tpm = tris(1-pyrazolyl)methane, bqdi = *o*-benzoquinonediimine) has been synthesised from 1,2-diaminobenzene and the precursor complex $Ru^{III}(tpm)Cl_3{\cdot}1.5H_2O$[17c] in the presence of NEt_3 as a base in absolute ethanol. The aqua derivative $[Ru^{II}(tpm)(bqdi)(H_2O)](ClO_4)_2$ ($[\mathbf{2}](ClO_4)_2$) was prepared from $[\mathbf{1}]ClO_4$ *via* a Cl/H_2O exchange reaction using $AgNO_3$ in 1:4 acetone-water mixture. The diamagnetic $[\mathbf{1}]ClO_4$ and $[\mathbf{2}](ClO_4)_2$ exhibit 1:1 and 1:2 conductivities, respectively, and give satisfactory microanalytical data. The mass spectra (ESI-MS(+)) of complexes $[\mathbf{1}]ClO_4$ and $[\mathbf{2}](ClO_4)_2$ show molecular ion peaks at 457.02 and 520.92 corresponding to $[[\mathbf{1}]ClO_4\text{-}ClO_4]^+$ and $[[\mathbf{2}](ClO_4)_2\text{-}ClO_4\text{-}H_2O]^+$, respectively, (Fig. S1† and Experimental). The complexes show characteristic $\nu(ClO_4)$ vibrations in the IR spectra near 1100/625 cm^{-1}.

The identities of $[\mathbf{1}]ClO_4$ and $[\mathbf{2}](ClO_4)_2$ have been authenticated by their single crystal X-ray structures (Figs. 1-2, Tables 1, 2 and S1†). The asymmetric unit of $[\mathbf{2}](ClO_4)_2$ contains two crystallographically independent molecules (**Molecule A** and **Molecule B**) with only slight difference in bond parameters.

The tridentate tpm ligand is coordinated to the metal ion in the usual facial mode as an N,N′,N″ donor, forming two shared six-membered chelate rings around the ruthenium ion. The bidentate bqdi is bonded to the ruthenium ion as an NH,NH′ donor, resulting in a five-membered chelate ring. The redox non-innocent feature of the quinonoid moiety, bqdi (fully oxidised quinone state ($bqdi^0$), intermediate semiquinone radical form ($bqdi^{\bullet -}$)

and fully reduced form (bqdi^{2-}),[3,14] and the facile access of various oxidation states of the ruthenium ion (Ru^{II}, Ru^{III}, Ru^{IV}) extend the feasibility of three valence configurations for [**1**]ClO$_4$ or [**2**](ClO$_4$)$_2$: {Ru^{II}-bqdi^0}, {Ru^{III}-bqdi$^{\bullet-}$}, or {Ru^{IV}-bqdi^{2-}}, as shown in Scheme 1. Since the coordinated quinonoid moieties are known to exhibit distinctive bond parameters depending on the redox state (e.g. C-NH distances, bqdi^0: 1.30 Å, bqdi$^{\bullet-}$: 1.35 Å, bqdi^{2-}: 1.38 Å),[22] an analysis of the relevant bond parameters of the complexes can therefore provide important information regarding the valence distribution at the metal-quinonoid interface. The close to double bond distances of HN1-C1, HN2-C6 (average, 1.318(5) Å; DFT: 1.318 Å), the short intra ring distances, C2-C3/C4-C5 (average, 1.349(5) Å; DFT: 1.364 Å), and the single bond distances for C1-C2, C3-C4, C5-C6, C6-C1 (average, 1.436 Å; DFT: 1.444 Å) of coordinated bqdi in [**1**]ClO$_4$ (Table 2) strongly suggest the {Ru^{II}-bqdi^0} configuration. Similarly, the corresponding sensitive bond parameters of coordinated bqdi in the analogous aqua derivative, [**2**](ClO$_4$)$_2$ (Table 2) also establish the {Ru^{II}-bqdi^0} configuration. The structure data rule out the possibility of other valence tautomeric forms, i.e. {Ru^{III}-bqdi$^{\bullet-}$} or {Ru^{IV}-bqdi^{2-}}.

The Ru^{II}-N(tpm/bqdi),[3g,17d,7a,14d] Ru^{II}-Cl[17d,21,4] and Ru^{II}-O(H$_2$O)[23] bond distances are in good agreement with those of related reported ruthenium(II) complexes. The bite angle of the five-membered chelate ring involving the bqdi ligand, N1-Ru1-N2 or N9-Ru2-N10, ~77° is slightly smaller than that of the six-membered chelate rings involving the tpm ligand, N3-Ru1-N5/N5-Ru1-N7/N3-Ru1-N7 or N11-Ru2-N15/ N13-Ru2-N15/ N11-Ru2-N13, ~82-88° (Table S1†).

The DFT calculated bond distances and angles (Tables 2, S1†) based on the optimised structures of $\mathbf{1}^+$ and $\mathbf{2}^{2+}$ (**Molecule A**) (Fig. S2†) are in fairly good agreement with the X-ray data. An open-shell singlet optimisation of $\mathbf{1}^+$ at the B3LYP level gives rise to the same energy as that obtained from the closed-shell singlet calculations which rules out a major contribution from the antiferromagnetically coupled $\{Ru^{III}\text{-bqdi}^{\bullet-}\}$ form, in agreement with the experimental information.

^{1}H NMR spectra of [**1**]ClO_4 in different solvents such as $CDCl_3$, $(CD_3)_2SO$, CD_3CN and $(CD_3)_2CO$ exhibit partially overlapping resonances, corresponding to 16 protons, within the chemical shift range of 14-5.5 ppm (Fig. S3(a)†). Though the solvent dependence of chemical shift values for the aromatic protons of tpm or bqdi is insignificant, some variations for the methine (CH) proton of tpm (9.11-10.02 ppm) and appreciable variations for the NH proton resonances of bqdi (11.48-13.64 ppm) have been observed due to the acidity of these protons (Fig. S3(a)†). The proton resonances of the corresponding aqua complex [**2**]$(ClO_4)_2$ in $(CD_3)_2CO$ are slightly upfield shifted with respect to those of chloro complex [**1**](ClO_4) (Fig. S3(a)†). The NH (bqdi) and CH (methine of tpm) protons of [**2**]$(ClO_4)_2$ disappear in D_2O due to H/D exchange. The aromatic ring protons of bqdi appear separately as an $AA^/BB^/$ system. The spin-spin coupling constant values (*J*) of the aromatic protons of tpm are rather small (Experimental), as reported earlier[3h,17d] which distinguish the protons associated with the coordinated tpm and bqdi ligands in the complexes. The ^{1}H NMR spectra show two disparate sets of pyrazol-1-yl resonances (Fig. S3(a)†, Experimental) of coordinated tpm with the peak integrals ratio of 2:1 corresponding to α′, β′, γ′ and α, β, γ protons, respectively (Scheme 2). The protons associated with the coordinated tpm and bqdi ligands in the complexes have been assigned based on the ^{1}H-^{1}H COSY and 1D-homonuclear NOE (Nuclear Overhauser Enhancement) difference experiments of representative $\mathbf{1}^+$ in CD_3CN (Fig. S3b-c†) as well as with respect to the reported NMR spectral features of analogous ruthenium-tpm complexes.[24] The cross peaks of the proton at δ 6.16 ppm with the protons at δ 8.18 ppm and δ 5.87 ppm in ^{1}H-^{1}H COSY (Fig. S3(b)†) suggest their correspondences to the H^β, H^γ and H^α, respectively (Scheme 2, Fig. S3(b)†). Also, the protons at δ 6.70 ppm (corresponding to $H^{\beta'}$) show cross peaks with the protons at δ 8.42 ppm and δ 8.44 ppm which correspond to $H^{\gamma'}$ and $H^{\alpha'}$ (Scheme 2, Fig. S3(b)†), respectively, since $^3J(H^{\beta'}H^{\gamma'}) > {}^3J(H^{\beta'}H^{\alpha'})$[24] (Experimental). Similarly, the bqdi protons at δ 7.36 ppm show cross peaks with the protons at δ 6.94 ppm (Scheme 2, Fig. S3(b)†). Further, NOE experiment was performed to differentiate between $H^{\gamma'}$and $H^{\alpha'}$ as well as H^γ and H^α protons (Scheme 2, Fig. S3(c)†). The enhancement in intensity of the peaks at δ 8.42 ppm and δ 8.18 ppm along with the disappearance of other peaks (Fig. S3(c)†) on irradiation at δ 9.11 ppm (corresponding to H^δ) implies their correspondences to $H^{\gamma'}$ and H^γ (Scheme 2), respectively. The assignment of peaks of tpm based on the criterion $^3J(H^{\beta'}H^{\gamma'}) > {}^3J(H^{\beta'}H^{\alpha'})$[24] has led to reveal the swapping of the chemical shift positions of $H^{\gamma'}$ and $H^{\alpha'}$ protons in CD_3CN with respect to those in other solvents (Fig. S3(a)†, Experimental). Therefore, NOE experiment was also carried out for representative $\mathbf{1}^+$ in $(CD_3)_2CO$ and it was found that on irradiation at δ 9.89 ppm, (corresponding to H^δ) the intensity of the peaks at δ 8.64 ppm and δ 8.45 ppm are enhanced (Fig. S3(d)†) which leads to their correspondences to $H^{\gamma'}$ and H^γ (Scheme 2), respectively, further validating the aforementioned criterion $^3J(H^{\beta'}H^{\gamma'}) > {}^3J(H^{\beta'}H^{\alpha'})$.[24]

Except H^{α} and H^{β} protons (Scheme 2), all other protons of tpm are deshielded on coordination to the metal ion. The deshielding may be due to the inductive effect[24a] exerted by the bqdi ligand whose nitrogen donors are *trans* to the donor atoms of the two magnetically equivalent pyrazol-1-yl groups. The H^{α} proton undergoes significant shielding due to its closeness to the bqdi ring, thus lying in the shielding cone of the bqdi ring. Some of the magnetic anisotropy[24a] effect has also been transmitted to the H^{β} proton which causes its little upfield shifting as compared to the uncoordinated ligand.

Electrochemistry, EPR, UV-vis spectroelectrochemistry, and DFT calculations of $\mathbf{1}^{n}$ (n = 2+, 1+, 0)

Complex [**1**]ClO$_4$ exhibits reversible 1e$^-$ oxidation and reduction processes at $E°_{298}$, V (ΔE_p, mV): 0.82(80) and -0.79(80) in CH_3CN *versus* SCE/0.1 M Et_4NClO_4 (Fig. 3). However, the second reduction at E_{pc}, V = -1.39 is irreversible in nature at the cyclic voltammetric time scale.

The orbital contributions to the MOs of $\mathbf{1}^{+}$ (Table S2†) predict that the HOMO is composed of 58% Ru with appreciable contribution from Cl (24%) which confirms metal based oxidation, $Ru^{II} \rightarrow Ru^{III}$, leading to the {$Ru^{III}$-bqdi^0} valence formalism for $\mathbf{1}^{2+}$. This is further supported by the DFT calculated C-NH bond distance of 1.312 Å (Table S5†) corresponding to a bqdi^0 state[22,14d] in $\mathbf{1}^{2+}$. The Mulliken spin density distribution in $\mathbf{1}^{2+}$ (Ru: 0.767, Cl: 0.173, tpm: 0.047, bqdi: 0.014 (Fig. 4a)) and 65% contribution of Ru in the β-LUMO of $\mathbf{1}^{2+}$ (Table S3†) are further in agreement with the {Ru^{III}-bqdi^0} configuration. Accordingly, the oxidised species ($\mathbf{1}^{2+}$) exhibits an anisotropic EPR spectrum[25] at 110 K in glassy frozen CH_3CN/0.1 M Bu_4NPF_6 with $g_1 = 2.463$, $g_2 = 2.248$,

g_3 = 1.883, $\langle g\rangle = [(1/3)(g_1^2 + g_2^2 + g_3^2)]^{1/2}$ = 2.211, and $\Delta g = g_1 - g_3$= 0.580 (Fig. 5a),[2a] suggesting largely metal-centred spin (Ru^{III}).

On the other hand, LUMO of **1**$^+$ is dominated by bqdi (68%) based orbitals (Table S2†) which suggests a bqdi based reduction resulting in the valence configuration of [Ru^{II}(tpm)(bqdi$^{\bullet-}$)(Cl)] for **1**. Consequently, α-SOMO of **1** (Table S4†) is dominated by bqdi (70%) based orbitals. In accordance, the DFT calculated C-NH bond distance of bqdi increases from 1.318 Å (corresponding to bqdi^0) to 1.342 Å (corresponding to bqdi$^{\bullet-}$) (Table S5†) on moving from **1**$^+$ to **1**. The presence of 23% Ru contribution in the LUMO of **1**$^+$ (Table S2†) implies appreciable (dπ)Ru^{II}→π*(bqdi^0) back-bonding.[14d] The Mulliken spin density distribution in **1** (bqdi: 0.857, Ru: 0.128, Cl: 0.008, tpm: 0.006 (Fig. 4b)) signifies that bqdi$^{\bullet-}$ is the primary spin bearing centre. This has been further corroborated by the experimentally obtained unresolved free radical EPR signal[3c-f] of the reduced species, **1** at g = 1.988 (Fig. 5b), pointing to a Ru^{II}-coordinated anion radical ligand.[2a]

In the visible region dissolved **1**$^+$ displays one weak absorption at 760 nm, followed by a moderately intense band at 514 nm besides other intense higher energy transitions in the UV region (Fig. 6, Table 3). The TD-DFT calculations on the optimised structure of **1**$^+$ in the S = 0 state also predict one weak transition (at 674 nm), followed by an intense transition at 480 nm, corresponding to mixed dπ(Ru^{II})→π*(bqdi^0)/dπ(Cl)→π*(bqdi^0) MLCT (metal-to-ligand charge transfer)/LLCT (ligand-to-ligand charge transfer) and dπ(Ru^{II})→π*(bqdi^0) MLCT transitions, respectively (Table 4).[14d] On the other hand, dπ(Ru^{II})→π*(tpm) based MLCT transitions appear only around 300 nm.[17d]

On one-electron oxidation of [Ru^{II}(tpm)(bqdi^0)(Cl)]$^+$ (**1**$^+$) to [Ru^{III}(tpm)(bqdi^0)(Cl)]$^{2+}$ (**1**$^{2+}$) the lowest energy band at 760 nm disappears and one weak band appears at 530 nm followed by two moderately intense nearby bands at 455 nm and 436 nm (Fig. 6, Table 3). TD-DFT calculations predict several transitions in that region which primarily consist of tpm(π)→Ru(dπ*) and tpm(π)→bqdi(π*) based LMCT (ligand-to-metal charge transfer) and LLCT (ligand-to-ligand charge transfer) transitions (Table 4).[3h] TD-DFT calculations also predict weak transitions at 600-800 nm which have not been observed experimentally (Fig. 6).

The one-electron reduced [Ru^{II}(tpm)(bqdi$^{\bullet-}$)(Cl)] (**1**) exhibits one weak band at 780 nm followed by one intense band at 637 nm and several moderately intense absorptions in the higher energy region. The transitions are assigned based on the TD-DFT calculations as MLCT transitions involving filled Ru^{II} and singly occupied bqdi$^{\bullet-}$ or empty tpm(π*) orbitals[3f] as well as inter-ligand transitions (Tables 3 and 4, Fig. 6).

The aqua complex [Ru^{II}(tpm)(bqdi^0)(H$_2$O)]$^{2+}$ (**2**$^{2+}$) in water displays one weak band at 720 nm, followed by an intense band at 497 nm which are assigned to Ru(dπ)→bqdi(π*) MLCT transitions based on the TD-DFT calculations (Table S6). A Ru(dπ)→tpm(π*) based absorption has been observed at higher energy, at 316 nm (Table S6 and Experimental). On moving from the chloro complex (**1**$^+$) to the corresponding aqua derivative (**2**$^{2+}$) the MLCT bands undergo blue shifts from 760 nm and 514 nm to 720 nm and 497 nm, respectively, due to the stabilisation of dπ orbitals of ruthenium.[26]

Besides the establishment of valence and spin configurations of the complexes, as discussed in the preceding sections, the study has further been extended to catalytic epoxidation of olefins. Unlike earlier reported isomeric complexes [Ru^{II}(trpy)(L)Cl] (trpy

= 2,2/:6/,2//-Terpyridine and HL = Quinaldic Acid),[21] the analogous chloro species $[Ru(tpm)(bqdi)Cl]^+$ (**1**$^+$) failed to show any epoxidation activity in presence of oxidants such as H_2O_2, ^tBuOOH or $PhI(OAc)_2$, possibly due to the lack of necessary lability of the chloro group. Therefore, the corresponding solvato species $[Ru(tpm)(bqdi^0)H_2O]^{2+}$ (**2**$^{2+}$) has been explored for its feasibility to function as a pre-catalyst for the epoxidation process.

Catalytic epoxidation reaction with system 2^n

The MOs of the DFT optimised aqua complex $[Ru^{II}(tpm)(bqdi^0)(H_2O)]^{2+}$ (**2**$^{2+}$) (Fig. S2, Table S7†) suggest that HOMO and HOMO-1 are primarily composed of metal based orbitals, 63% and 70%, respectively. Accordingly, **2**$^{2+}$ exhibits two successive metal based oxidation processes at 0.44 V and 0.64 V in buffer solution of pH~7 (Fig. S4†) which may lead to the eventual formation of a $\{Ru^{IV}{=}O\}$ species as shown in eqns. (1) and (2).[21q,r]

$$[Ru^{II}(tpm)(bqdi^0)(H_2O)]^{2+} \rightarrow [Ru^{III}(tpm)(bqdi^0)(OH)]^{2+} + H^+ + e^- \qquad (1)$$

$$[Ru^{III}(tpm)(bqdi^0)(OH)]^{2+} \rightarrow [Ru^{IV}(tpm)(bqdi^0)(O)]^{2+} + H^+ + e^- \qquad (2)$$

The aqua complex (**2**$^{2+}$) has thus been tested as a pre-catalyst for the epoxidation of a wide variety of alkene functionalities using $PhI(OAc)_2$ as the oxidant in CH_2Cl_2 solution under aerobic reaction conditions at 298 K. The data for the epoxidation results are summarised in Table 5. Terminal alkenes were found to be the most effective substrates towards the said epoxidation process, except for α-methyl styrene where “over-oxidised” acetophenone is found to be the sole product (Table 5).

The addition of $PhI(OAc)_2$ to the CH_2Cl_2 solution of $\mathbf{2}^{2+}$ leads to the spontaneous change in colour of the solution from reddish orange to yellow due to the *in situ* formation of the corresponding ruthenium-oxo species $[Ru^{IV}(tpm)(bqdi)(O)]^{2+}$ ($\mathbf{3}^{2+}$) as has also been evidenced from the change in the UV-vis spectral features: a shift from 500 nm to 445 nm (Fig. S5†).[21r,27] The *in situ* generation of the oxo-species has further been established *via* the following experiments:

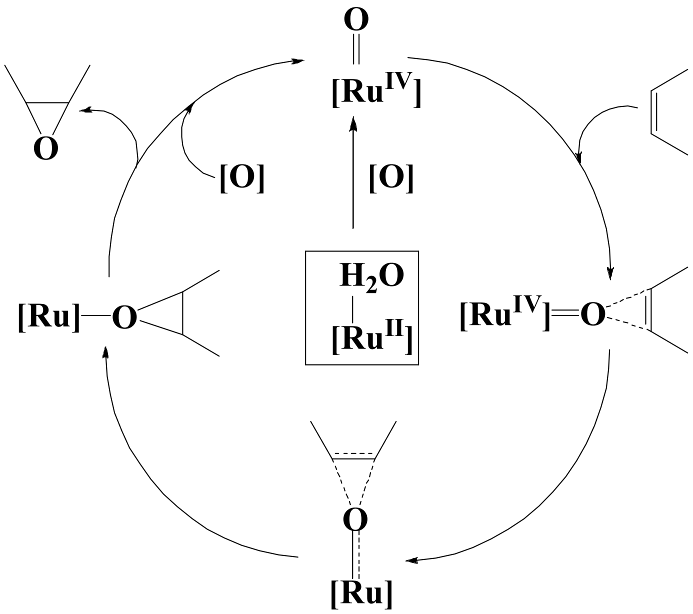
(i) On addition of methyl *p*-tolyl sulfide to the above yellow solution the colour of the solution reverts back to the initial reddish orange and the MLCT band of the aqua species at 500 nm re-appears (Fig. S5†) which suggests the oxidation of sulfide to sulfoxide with the concomitant reduction of $[Ru^{IV}(tpm)(bqdi)(O)]^{2+}$ ($\mathbf{3}^{2+}$) to $[Ru^{II}(tpm)(bqdi)(H_2O)]^{2+}$ ($\mathbf{2}^{2+}$). The conversion of *p*-tolyl sulfide to *p*-tolyl sulfoxide instead of possible *p*-tolyl sulfone has been confirmed by GC experiments.

(ii) The addition of PPh_3 to the $CDCl_3$ solution of $\mathbf{2}^{2+}$ in the presence of stoichiometric amounts of $PhI(OAc)_2$ results in the *in situ* formation of $O{=}PPh_3$, as confirmed by the ^{31}P NMR spectrum of the resulting solution which displays a peak at ~30 ppm, typical of $O{=}PPh_3$ (Fig. S6†).[21r]

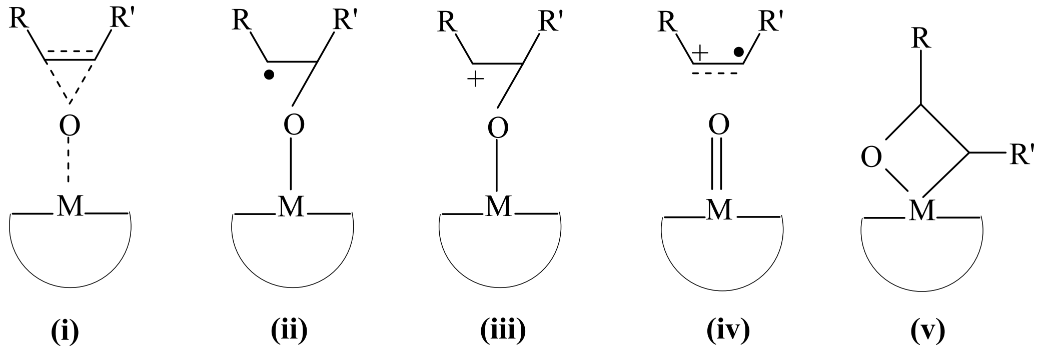
(iii) The peak at *m/Z* (*Z* = 2) 331.04 (Fig. S1†) in the mass spectrum, obtained on addition of $PhI(OAc)_2$ to the mixture of $[\mathbf{2}](ClO_4)_2$ and styrene in CH_2Cl_2 suggests the *in situ* formation of an adduct between $[Ru^{IV}(tpm)(bqdi)(O)]^{2+}$ and styrene.[21r]

The fully oxidised form of the "non-innocent" quinonoid ligand (bqdi^0) in the precursor aqua complex (**2**$^{2+}$) allows the ruthenium ion to adopt a higher oxidation state *via* the formation of an oxo-species in the presence of a suitable oxidant, PhI(OAc)$_2$, which in turn makes it highly electrophilic to react with the incoming alkene functionalities. Consequently, DFT calculations on the optimised ruthenium-oxo species, [Ru^{IV}(tpm)(bqdi^0)(O)]$^{2+}$ (**3**$^{2+}$) (Fig. 7) reveal that the triplet (S = 1) state is more stable (~21 kcal mol^{-1}) than the corresponding singlet (S = 0) ground state.

Metal complex catalysed epoxidation of alkenes is known to proceed *via* the formation of an active metal-oxo intermediate through the mediation of a suitable oxidant. The electrophilic metal bound oxo group subsequently interacts with the incoming olefinic double bond with eventual transfer of the oxo group[19,21] to the olefin as shown in Scheme 3.



Scheme 3. Proposed reaction pathway.



Scheme 4. Possible transition states/intermediates for the transfer of oxygen from the metal-oxo species to the olefinic double bond.

It has been proposed earlier that the transfer of oxygen atom from the metal-oxo complex to the olefinic double bond can proceed *via* any of the following five possible different pathways: (i) concerted transition state, (ii) carbon radical, (iii) carbocation, (iv) π-radical cation, (v) metalaoxetane (Scheme 4).[21r,28,29]

However, DFT calculations on the optimised adduct (**A**, Fig. 7) comprising of a ruthenium-oxo species (**3**$^{2+}$) and styrene as the model substrate reveal that the concerted transition state pathway is preferred in the present case. Upon approach of styrene towards the ruthenium-oxo species, the Ru-O1 bond length increases to 2.17 Å from 1.78 Å while the C_α-C_β bond of styrene lengthens to 1.44 Å from the standard carbon-carbon double bond length of ~1.34 Å, with the simultaneous formation of C_α-O1 and C_β-O1 bonds (Fig. 7, Table S8†). These in effect alter the electronic property of **A** with respect to the intermediate oxo complex. Thus, the natural charge on Ru decreases to 0.62 from 0.89 and that on O1 increases to -0.56 from -0.26, implying less electrophilic character of the Ru-O bond in **A** as has also been reflected by the single bond character of the Ru-O1 bond (Table S8†). The absence of α and/or β spin on the C_α-C_β bond rules out the possibility of formation of the other alternatives, **ii-iv,** in Scheme 4. The spin density analysis of the adduct (**A**) and the intermediate oxo-species reveals a large delocalisation of charge around the Ru-bqdi plane in **A** while in the oxo-species it is rather localised on the Ru-O1 bond (Ru: 0.83 and O1: 1.11) (Fig. 8). The complete disappearance of spin on O1 provides the necessary justification in favor of the existence of transition state "**i**" in the present case (Scheme 4). Moreover, energy calculations reconfirm that "**i**" (Scheme 4) is situated only ~8 kcal mol^{-1} higher than the pre-catalyst, $\mathbf{2}^{2+}$.

The formation of a concerted transition state **"i"** (Scheme 4) has also been supported by a ^{19}F NMR spectral study in the case of 4-fluorostyrene as the substrate where the peak of free 4-fluorostyrene at −114 ppm remains unchanged on addition of PhI(OAc)$_2$ to the reaction mixture containing the substrate 4-fluorostyrene and the pre-catalyst $\mathbf{2}^{2+}$ in CDCl$_3$. The existence of any of the other intermediates, **ii-iv**, in Scheme 4 would have resulted in shifting along with broadening, due to the paramagnetic nature of the alkene, of the peak during the said catalytic process.

Conclusion

The experimental and DFT calculations establish that the redox non-innocent *o*-benzoquinonediimine (bqdi) has been stabilised in its fully oxidised quinone state in both the chloro complex ($[\mathrm{Ru^{II}(tpm)(bqdi^{0})(Cl)}]^{+}$) (**1**$^{+}$) and in the aqua ($[\mathrm{Ru^{II}(tpm)(bqdi^{0})(H_2O)}]^{2+}$) derivative (**2**$^{2+}$). The chloro complex exhibits metal based oxidation: $[\mathrm{Ru^{II}(tpm)(bqdi^{0})(Cl)}]^{+}$ (**1**$^{+}$)$\rightarrow[\mathrm{Ru^{III}(tpm)(bqdi^{0})(Cl)}]^{2+}$ (**1**$^{2+}$) and bqdi centred reduction ($[\mathrm{Ru^{II}(tpm)(bqdi^{0})(Cl)}]^{+}$ (**1**$^{+}$)$\rightarrow[\mathrm{Ru^{II}(tpm)(bqdi^{\bullet-})(Cl)}]$ (**1**)). The aqua complex **2**$^{2+}$ functions as an efficient pre-catalyst for the selective epoxidation of a wide variety of alkenes in the presence of $\mathrm{PhI(OAc)_2}$ as the sacrificial oxidant in $\mathrm{CH_2Cl_2}$ where the oxidation proceeds through an inferred intermediate oxo-species $[\mathrm{Ru^{IV}(tpm)(bqdi^{0})(O)}]^{2+}$ (**3**$^{2+}$). Terminal alkenes are found to be the most effective substrates, except α-methyl styrene where "over-oxidised" acetophenone is found to be the sole product. The mechanistic pathway for the epoxidation process has been deciphered *via* DFT calculations which suggest the involvement of a concerted transition state.

Experimental

Materials

The ligand tris(1-pyrazolyl)methane (tpm)[17b] and the starting material [Ru(tpm)(Cl)$_3$].1.5H$_2$O[17c] were prepared as reported previously in the literature. The chemicals and solvents were of reagent grade and used as received. Deionised water of high purity was obtained by passing distilled water through a nanopure Milli-Q water purification system. For solution of pH 7.0 a hydrogen phosphate/dihydrogen phosphate buffer was employed. For spectroscopic and electrochemical studies, HPLC grade solvents were employed.

Physical Measurements

Electrical conductivities were checked using a Systronic conductivity bridge 305. Solid state infrared spectra with samples prepared as KBr pellets were taken on a Nicolet spectrophotometer. ^{1}H NMR, ^{1}H-^{1}H COSY, 1D-homonuclear NOE, ^{31}P NMR and ^{19}F NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. Electrochemical measurements were carried out using a PAR model 273A electrochemistry system. Platinum wire working and auxiliary electrodes and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. The supporting electrolyte was 0.1 mol dm^{-3} Et$_4$NClO$_4$ and the solute concentration was ~ 10^{-3} mol dm^{-3}. The half-wave potential E^{o}_{298} was set equal to 0.5(E_{pa} + E_{pc}), where E_{pa} and E_{pc} are anodic and cathodic cyclic voltammetric peak potentials, respectively. A glassy carbon electrode was used for the electrochemical measurements of [**2**](ClO$_4$)$_2$. A Perkin-Elmer Lambda 950 spectrophotometer was used for recording the spectra of **1**$^+$

and $\mathbf{2}^{2+}$. UV-vis spectroelectrochemical studies were performed in CH_3CN / 0.1 mol dm^{-3} Bu_4NPF_6 at 298 K using an optically transparent thin-layer electrode (OTTLE) cell[30] mounted in the sample compartment of a J&M TIDAS spectrophotometer. All the spectroelectrochemical experiments were performed under dinitrogen atmosphere. The EPR measurements were made in a two electrode capillary tube[31] with an X-band (9.5 GHz) Bruker system ESP300 spectrometer. Elemental analyses were done on Perkin-Elmer 240C elemental analyser. Micromass Q-ToF mass spectrometer was used for recording electrospray mass spectra. The catalytic reactions were monitored using gas chromatographic techniques on Shimadzu GC-2014 gas chromatograph with an FID detector using a capillary column (112-2562 CYCLODEXB, from J&W Scientific, length 60 m, inner diameter 0.25 mm, film 0.25 μm).

Crystallography

Single crystals of [**1**]$ClO_4.2H_2O$ and 2([**2**]$(ClO_4)_2$).H_2O were grown by slow evaporation of 1:3 acetonitrile-toluene and 1:3 H_2O-toluene solutions, respectively. The structures were solved and refined by full-matrix least-squares techniques on F^2 using the SHELX-97 program.[32] The absorption corrections were done by the multi-scan technique. All data were corrected for Lorentz and polarisation effects, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement process as per the riding model. Hydrogen atoms of the two H_2O molecules in the unit cell of [**1**]ClO_4 could not be located, however, these have been included in the composition in Table 1.

CCDC numbers for [**1**]$ClO_4.2H_2O$ and 2([**2**]$(ClO_4)_2$).H_2O are 904797 and 904798, respectively.

Computational details

Full geometry optimisations were carried out at the (R)B3LYP and (U)B3LYP levels[33,34] for $\mathbf{1}^{+}$, $\mathbf{2}^{2+}$ and $\mathbf{1}^{2+}$, **1**, $\mathbf{3}^{2+}$, respectively, using the density functional theory method with Gaussian 03 (revision C.02).[35] All elements except ruthenium were assigned the 6-31G(d) basis set. The LANL2DZ basis set with the effective core potential was employed for the ruthenium atom.[36,37] Vertical electronic excitations based on B3LYP optimised geometries were computed for the time-dependent density functional theory (TD-DFT) formalism[38] in acetonitrile using the polarisable continuum model (PCM) of Tomasi and co-workers; specifically, the conductor like PCM (CPCM) in conjugation with the united atom topological model (using UAO radii, implemented in Gaussian 03) was applied.[39-41] GaussSum[42] was used to calculate the fractional contributions of various groups to each molecular orbital. No symmetry constraints were imposed during structural optimisations, and the nature of the optimised structures and energy minima were defined by subsequent frequency calculations. Natural bond orbital (NBO) analyses were performed using the NBO 3.1 module of Gaussian 03 on optimised geometry.[43] All the calculated structures were visualised with ChemCraft.[44]

General procedure for catalytic epoxidation studies

The pre-catalyst [**2**]$(ClO_4)_2$ (1.50 mg, 0.0016 mmol) in 5 cm^3 CH_2Cl_2 was taken in a glass vial and stirred for 15 min at 298 K. The olefin (0.24 mmol) followed by the oxidant iodobenzene diacetate (0.64 mmol) were added to the above solution under continuous stirring condition at 298 K. The progress of the reaction was monitored by gas chromatography. The conversions were determined from the gas chromatograms using standard samples and/or ^{1}H NMR.

Preparation of complexes

Synthesis of [Ru(tpm)(bqdi)(Cl)]ClO_4 ([1]ClO_4). Ru(tpm)$(Cl)_3$ (100 mg, 0.24 mmol) and 1,2-phenylenediamine (38.93 mg, 0.36 mmol) were taken in 25 cm^3 ethanol and NEt_3 (0.1 cm^3, 0.72 mmol) was added to the mixture. The mixture was heated to reflux with constant stirring for 6 h which resulted in a pink solution. The removal of solvent under reduced pressure yielded a dark coloured solid mass. The solid mass was dissolved in minimum volume of acetonitrile and saturated aqueous $NaClO_4$ solution was added to it and it was kept in a refrigerator overnight. The residue thus obtained on filtration was washed with minimum volume of chilled water and then dried in vacuo over P_4O_{10}. The crude solid was purified using a silica gel (60-120 mesh) column. The pink band corresponding to [**1**]ClO_4 was eluted by 5:1 dichloromethane-acetonitrile mixture. Evaporation of the solvent mixture under reduced pressure yielded the pure complex [**1**]ClO_4. Yield: 79 mg (60%). Anal. Calcd for $C_{16}H_{16}N_8Cl_2O_4Ru$: C, 34.54; H, 2.90; N, 20.15. Found: C, 34.62; H, 2.80; N, 19.95. Molar conductivity (Λ_M (Ω^{-1} cm^2 dm^3 mol^{-1}), CH_3CN): 140. ESI-MS(+) (*m/Z*, CH_3CN): 457.02 (Calcd 457.02 for [Ru(tpm)(bqdi)(Cl)]$^+$). IR (cm^{-1}, KBr pellet): 1119, 622 (corresponding to $\nu(ClO_4^-)$). ^{1}H NMR: (400 MHz): δ (ppm): $CDCl_3$: 11.48 (2H, s, NH), 10.02 (1H, s, H^{δ}), 8.58 (2H, d, ^3J ($H^{\beta'}H^{\gamma'}$) 2.92 Hz, $H^{\gamma'}$), 8.46 (1H, d, ^3J ($H^{\beta}H^{\gamma}$) 3.56 Hz, H^{γ}), 8.45 (2H, d, ^3J ($H^{\beta'}H^{\alpha'}$) 2.24 Hz, $H^{\alpha'}$), 7.34 (2H, dd, J 7.11, 3.11 Hz, H^a), 6.99 (2H, dd, J 7.00, 3.12 Hz, H^b), 6.66 (2H, pseudo t, $H^{\beta'}$), 6.13 (1H, pseudo t, H^{β}), 5.72 (1H, d, ^3J ($H^{\alpha}H^{\gamma}$) 2.16 Hz, H^{α}); $(CD_3)_2SO$:

13.64 (2H, s, NH), 9.81 (1H, s, H$^{\delta}$), 8.59 (2H, d, ^3J (H$^{\beta'}$H$^{\gamma'}$) 2.82 Hz, H$^{\gamma'}$), 8.45 (2H, d, ^3J (H$^{\beta'}$H$^{\alpha'}$) 2.16 Hz, H$^{\alpha'}$), 8.36 (1H, d, ^3J (H$^{\beta}$H$^{\gamma}$) 2.84 Hz, H$^{\gamma}$), 7.38 (2H, dd, J 6.56, 2.92 Hz, H^{a}), 6.94 (2H, dd, J 7.04, 3.16 Hz, H^{b}), 6.86 (2H, pseudo t, H$^{\beta'}$), 6.26 (1H, pseudo t, H$^{\beta}$), 5.96 (1H, d, ^3J (H$^{\alpha}$H$^{\gamma}$) 2.20 Hz, H$^{\alpha}$); CD_3CN: 12.48 (2H, s, NH), 9.11 (1H, s, H$^{\delta}$), 8.44 (2H, d, ^3J (H$^{\beta'}$H$^{\alpha'}$) 2.24 Hz, H$^{\alpha'}$), 8.42 (2H, d, ^3J (H$^{\beta'}$H$^{\gamma'}$) 2.84 Hz, H$^{\gamma'}$), 8.18 (1H, d, ^3J (H$^{\beta}$H$^{\gamma}$) 2.88 Hz, H$^{\gamma}$), 7.36 (2H, dd, J 6.92, 3.16 Hz, H^{a}), 6.94 (2H, dd, J 6.88, 2.92 Hz, H^{b}), 6.70 (2H, pseudo t, H$^{\beta'}$), 6.16 (1H, pseudo t, H$^{\beta}$), 5.87 (1H, d, ^3J (H$^{\alpha}$H$^{\gamma}$) 1.92 Hz, H$^{\alpha}$); $(CD_3)_2CO$: 13.26 (2H, s, NH), 9.89 (1H, s, H$^{\delta}$), 8.64 (2H, d, ^3J (H$^{\beta'}$H$^{\gamma'}$) 2.84 Hz, H$^{\gamma'}$), 8.54 (2H, d, ^3J (H$^{\beta'}$H$^{\alpha'}$) 2.20 Hz, H$^{\alpha'}$), 8.45 (1H, d, ^3J (H$^{\beta}$H$^{\gamma}$) 2.96 Hz, H$^{\gamma}$), 7.46 (2H, dd, J 7.22, 2.98 Hz, H^{a}), 6.98 (2H, dd, J 7.00, 3.2 Hz, H^{b}), 6.81 (2H, pseudo t, H$^{\beta'}$), 6.31 (1H, pseudo t, H$^{\beta}$), 6.12 (1H, d, ^3J (H$^{\alpha}$H$^{\gamma}$) 2.20 Hz, H$^{\alpha}$). λ/nm (ε / dm^3 mol^{-1} cm^{-1}) in CH_3CN: 760 (420), 514 (12200), 332 (3090, sh), 302 (5550, sh), 216 (9680).

Synthesis of [Ru(tpm)(bqdi)(H_2O)](ClO_4)$_2$ ([2](ClO_4)$_2$). [**1**]ClO_4 (100 mg, 0.18 mmol) was taken in 25 cm^3 acetone-water (1:4) and $AgNO_3$ (306 mg, 1.8 mmol) was added to it. The mixture was heated to reflux under stirring condition for 4 h. The pink solution turned to reddish orange with the precipitation of AgCl. The mixture was then cooled to room temperature and the AgCl precipitate was filtered off through a sintered glass crucible G4. $NaClO_4$ was added to the concentrated filtrate (5 cm^3) and it was then refrigerated overnight. The solid [**2**](ClO_4)$_2$ thus obtained was filtered off and washed with a few drops of chilled water and dried in vacuo over P_4O_{10}. Yield: 99 mg (87%). Anal. Calcd for $C_{16}H_{18}N_8Cl_2O_9Ru$: C, 30.10; H, 2.85; N, 17.56. Found: C, 29.95; H, 2.80; N, 17.32%. Molar conductivity (Λ_M (Ω^{-1} cm^2 dm^3 mol^{-1}), H_2O): 225. ESI-MS(+) (*m/Z*,

H_2O): 520.9 (Calcd 520.8 for {[Ru(tpm)(bqdi)]ClO_4}$^+$). IR (cm^{-1}, KBr pellet): 3425, 1632 (corresponding to ν(OH)); 1092, 625 (corresponding to ν(ClO_4^-)). ^{1}H NMR: (400 MHz): δ (ppm): $(CD_3)_2CO$: 13.54 (2H, s, NH), 9.96 (1H, s, H^{δ}), 8.78 (2H, d, ^3J ($H^{\beta'}H^{\gamma'}$) 2.76 Hz, $H^{\gamma'}$), 8.69 (2H, d, ^3J ($H^{\beta'}H^{\alpha'}$) 1.96 Hz, $H^{\alpha'}$), 8.47 (1H, d, ^3J ($H^{\beta}H^{\gamma}$) 2.90 Hz, H^{γ}), 7.51 (2H, dd, J 7.14, 3.18 Hz, H^{a}), 7.05 (2H, dd, J 7.12, 3.20 Hz, H^{b}), 6.92 (2H, pseudo t, $H^{\beta'}$), 6.30 (2H, m, H^{β}, H^{α}); D_2O: 8.43 (2H, d, ^3J ($H^{\beta'}H^{\gamma'}$) 2.80 Hz, $H^{\gamma'}$), 8.39 (2H, d, ^3J ($H^{\beta'}H^{\alpha'}$) 2.24 Hz, $H^{\alpha'}$), 8.10 (1H, d, ^3J ($H^{\beta}H^{\gamma}$) 2.96 Hz, H^{γ}), 7.38 (2H, dd, J 7.10, 3.10 Hz, H^{a}), 6.96 (2H, dd, J 7.10, 3.10 Hz, H^{b}), 6.75 (2H, pseudo t, $H^{\beta'}$), 6.10 (1H, pseudo t, H^{β}), 5.79 (1H, br s, H^{α}). λ/nm (ε/dm^3 mol^{-1} cm^{-1}) in CH_3CN: 720 (1210), 497 (19800), 316 (5500, sh), 274 (13070, sh), 267 (13800, sh), 255 (14390).

(*CAUTION!* Perchlorate salts of metal complexes are generally explosive. Care needs to be taken while handling such complexes).

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Table 1 Selected crystallographic data for [**1**](ClO_4).$2H_2O$ and 2([**2**](ClO_4)$_2$).H_2O

	[**1**](ClO_4).$2H_2O$	2([**2**](ClO_4)$_2$).H_2O
Formula	$C_{16}H_{20}Cl_2N_8O_6Ru$	$C_{32}H_{38}Cl_4N_{16}O_{19}Ru_2$
M_r	592.36	1294.72
Crystal size/mm	0.23 x 0.19 x 0.15	0.33 x 0.28 x 0.23
Crystal system	Orthorhombic	Monoclinic
Space group	*P b c a*	$P2_1/c$
α / Å	16.7114(8)	15.2839(6)
β / Å	14.7773(8)	16.3749(8)
γ / Å	17.6340(14)	18.4186(8)
α (°)	90	90
β (°)	90	90.073(4)
γ (°)	90	90
V / Å^3	4354.7(5)	4609.7(4)
Z	8	4
μ / mm^{-1}	1.019	0.982
T / K	150(2)	150(2)
hkl range	-19 to 19, -16 to 17, -20 to 20	-18 to 18, -17 to 19, -21 to 21
ρ_{calcd} / mg m^{-3}	1.807	1.866
F(000)	2384	2600
2θ range (°)	6.72 to 50.00	6.66 to 50.00
Reflns collected	28203	39749
Unique reflns (R_{int})	3826 (0.0725)	8103 (0.0914)
Data/restraints/parameters	3826/0/298	8103/3/683
R_1 [$I > 2\sigma(I)$]	0.0404	0.0452
wR_2 (all data)	0.1194	0.0964

GOF on F^2	1.077	0.912
largest difference in peak and hole / e Å^{-3}	1.533 and -0.829	1.220 and -0.730

Table 2 Experimental (X-ray) and DFT calculated selected bond distances (Å) of $\mathbf{1}^{+}$ and $\mathbf{2}^{2+}$

	$\mathbf{1}^{+}$		$\mathbf{2}^{2+}$	
	X-ray	DFT	X-ray	DFT (**Molecule A**)
Ru(1)–N(1)	1.987(3)	2.020	1.990(5)	2.057
Ru(1)–N(2)	1.972(3)	2.020	1.972(5)	2.048
Ru(1)–N(3)	2.091(3)	2.139	2.069(4)	2.125
Ru(1)–N(5)	2.042(3)	2.127	2.018(4)	2.075
Ru(1)–N(7)	2.075(3)	2.139	2.080(4)	2.136
Ru(1)–Cl(1)	2.384(11)	2.405	-	-
Ru(1)–O(1)	-	-	2.128(5)	2.209
Ru(2)–N(9)	-	-	2.005(4)	-
Ru(2)–N(10)	-	-	1.991(4)	-
Ru(2)–N(11)	-	-	2.077(4)	-
Ru(2)–N(13)	-	-	2.027(4)	-
Ru(2)–N(15)	-	-	2.086(4)	-
Ru(2)–O(2)	-	-	2.110(4)	-
C(1)–N(1)	1.313(5)	1.318	1.317(7)	1.315
C(6)–N(2)	1.324(5)	1.318	1.316(7)	1.313
C(17)–N(9)	-	-	1.316(6)	-
C(22)–N(10)	-	-	1.299(7)	-
C(1)–C(2)	1.429(5)	1.434	1.433(7)	1.437
C(2)–C(3)	1.354(5)	1.364	1.353(8)	1.362
C(3)–C(4)	1.434(6)	1.442	1.419(8)	1.450
C(4)–C(5)	1.344(5)	1.364	1.349(8)	1.361
C(5)–C(6)	1.427(5)	1.434	1.425(7)	1.438
C(6)–C(1)	1.452(5)	1.468	1.456(8)	1.483
C(17)–C(18)	-	-	1.426(7)	-

C(18)–C(19)	-	-	1.351(7)	-
C(19)–C(20)	-	-	1.442(8)	-
C(20)–C(21)	-	-	1.335(8)	-
C(21)–C(22)	-	-	1.434(7)	-
C(22)–C(17)	-	-	1.448(7)	-

Table 3 UV-vis data for $\mathbf{1}^n$ (n = 2+, 1+, 0) from OTTLE spectroelectrochemistry in acetonitrile

Compound	λ/nm (ε/dm^{3}mol^{-1}cm^{-1})
$\mathbf{1}^{2+}$	217(10450), 272(3920), 302(3690), 436(10060), 455(10310), 530(1950)
$\mathbf{1}^{+}$	216(9680), 264 (8210), 302(5550, sh), 332(3090, sh), 514(12220), 760(420)
1	217(11450), 264(7770), 323(6040), 370(4460, sh), 449(4420), 637(6200), 780(880)

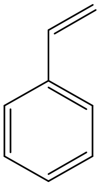
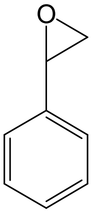
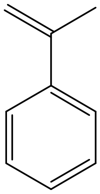
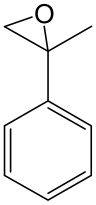
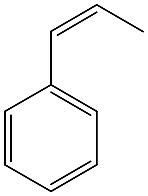
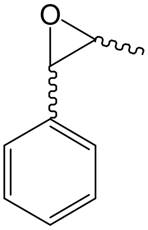
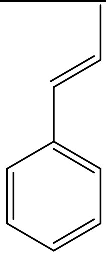
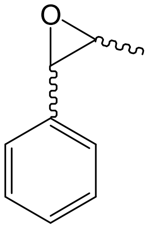
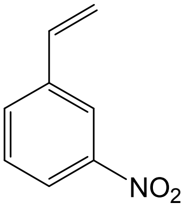
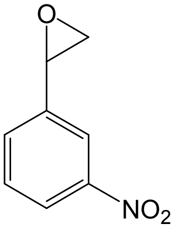
Table 4 TD-DFT calculated electronic transitions of $\mathbf{1}^n$ (n = 2+, 1+, 0)

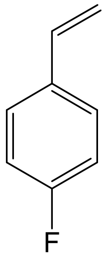
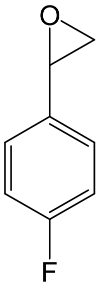
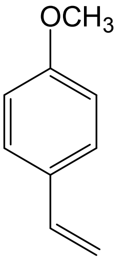
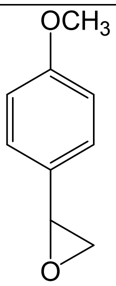
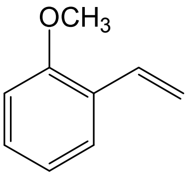
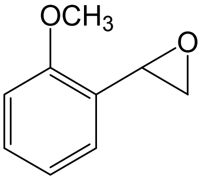
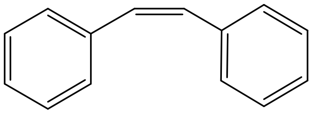
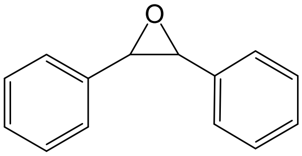
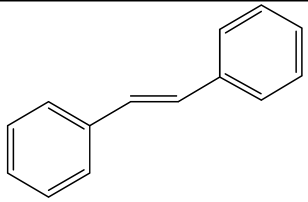
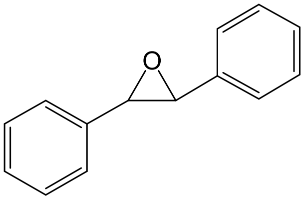
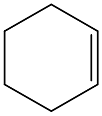
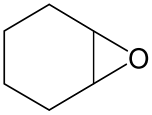
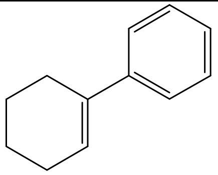
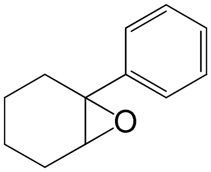
Energy/ eV	λ/nm	f^a	$\lambda_{\text{expt.}}$/nm (ε/dm^{3}mol^{-1}cm^{-1})	Transition	Character
			n=1+ (*S*=0)		
1.84	674.39	0.0110	760(420)	HOMO-2→LUMO (0.49) HOMO-1→LUMO (0.46)	Ru(dπ)→bqdi(π*) Cl(dπ)→bqdi(π*) Ru(dπ)→bqdi(π*)
2.58	479.69	0.2493	514(12220)	HOMO-2→LUMO (0.44)	Ru(dπ)→bqdi(π*)
3.61	343.52	0.0043	333(3090)	HOMO-1→LUMO+4 (0.48)	Ru(dπ)→tpm(π*)
3.99	310.63	0.0580	264(8210)	HOMO→LUMO+2 (0.57)	Ru(dπ)→tpm(π*)
			n=2+ (*S*=1/2)		
2.34	528.98	0.0063	530(1950)	HOMO-8(β)→LUMO(β) (0.63)	tpm(π)→Ru(dπ*)
2.61	474.63	0.0558	455(10310)	HOMO-5(β)→LUMO(β) (0.87)	tpm(π)→Ru(dπ*)
2.66	465.33	0.0297	436(10060)	HOMO-4(α)→LUMO(α) (0.83)	tpm(π)→bqdi(π*)
2.71	457.76	0.0050	436(10060)	HOMO-6(β)→LUMO(β) (0.88)	tpm(π)→Ru(dπ*)
			n=0 (*S*=1/2)		
1.89	655.52	0.0282	780(880)	HOMO-1(β)→LUMO(β) (0.87)	Ru(dπ)→bqdi(π*)
2.27	546.98	0.1443	637(6200)	HOMO-2(β)→LUMO(β) (0.85)	bqdi(π)→bqdi(π*) Cl(pπ)→bqdi(π*)
2.47	502.51	0.0118	449(4420)	HOMO-3(β)→LUMO(β) (0.98)	Ru(dπ)→bqdi(π*)
3.08	401.98	0.0081	370(4460)	HOMO-1(α)→LUMO(α) (0.91)	Ru(dπ)→tpm(π*)

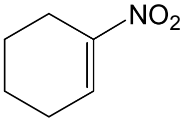
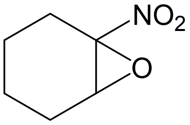
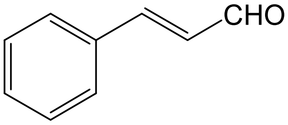
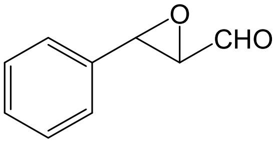
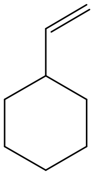
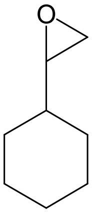
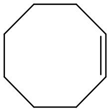
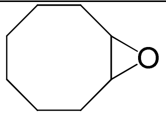
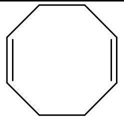
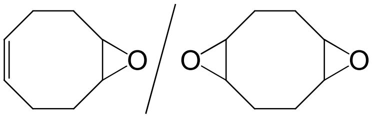
3.83	323.31	0.0355	323(6040)	HOMO-1(α)→ LUMO+2(α) (0.50)	Ru(dπ)→tpm(π*)

[a] Oscillator strength

Table 5 Catalysis results[a]

Substrate	Product	% Conversion	% Selectivity
		100	100
		100	0[b]
		97	100 (*cis*)
		97	64 (*trans*)
		100	100

		98	100
		100	71
		100	51
		100	96
		100	100
		99	100
		96	95

		100	100
		100	100
		95	52
		99	98
		100	2 / 98

[a]Detailed reaction condition is given in the experimental section. Products are characterised by GC, GC-MS and ^{1}H NMR.

[b]Acetophenone is the exclusive product.

Figure Caption:

Fig. 1 Crystal structure of [**1**]$ClO_4.2H_2O$. Ellipsoids are drawn at 50% probability level. Hydrogen atoms (except N-H protons), counter anion (ClO_4^-) and H_2O molecules are removed for clarity.

Fig. 2 Crystal structure of 2{[**2**]$(ClO_4)_2$}.H_2O. The asymmetric unit consists of two crystallographically independent molecules (**Molecule A** and **Molecule B**). Ellipsoids are drawn at 50% probability level. Hydrogen atoms (except N-H and O-H protons), counter anions (ClO_4^-) and water of crystallisation are removed for clarity.

Fig. 3 Cyclic voltammogram of [**1**]ClO_4 in CH_3CN/0.1 mol dm^{-3} Et_4NClO_4 *versus* SCE. Inset shows the reversible oxidation and first reduction couples.

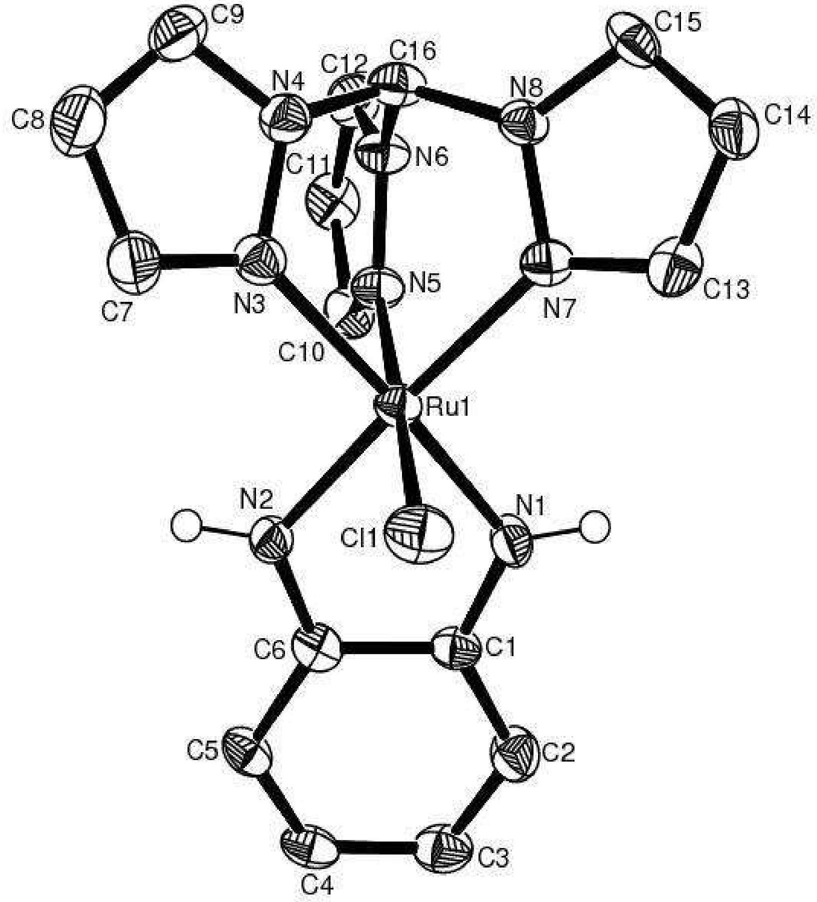
Fig. 4 Mulliken spin density plots of (a) $\mathbf{1}^{2+}$ and (b) **1**.

Fig. 5 EPR spectra of (a) $\mathbf{1}^{2+}$ at 110 K and (b) **1** at 298 K in CH_3CN/Bu_4NPF_6.

Fig. 6 UV-vis spectroelectrochemistry for $\mathbf{1}^{n}$ (n = 2+, 1+, 0) in CH_3CN/0.1 mol dm^{-3} Bu_4NPF_6.

Fig. 7 DFT optimised structures of (a) $[Ru(tpm)(bqdi)(O)]^{2+}$ ($\mathbf{3}^{2+}$) and (b) adduct (**A**) of $\mathbf{3}^{2+}$ and styrene.

Fig. 8 Spin density plots of (a) $[Ru(tpm)(bqdi)(O)]^{2+}$ ($\mathbf{3}^{2+}$) and (b) adduct (**A**) of $\mathbf{3}^{2+}$ and styrene.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C15
C12
C16
N4
N8
C8
C14
N6
C11
C7
N3
N5
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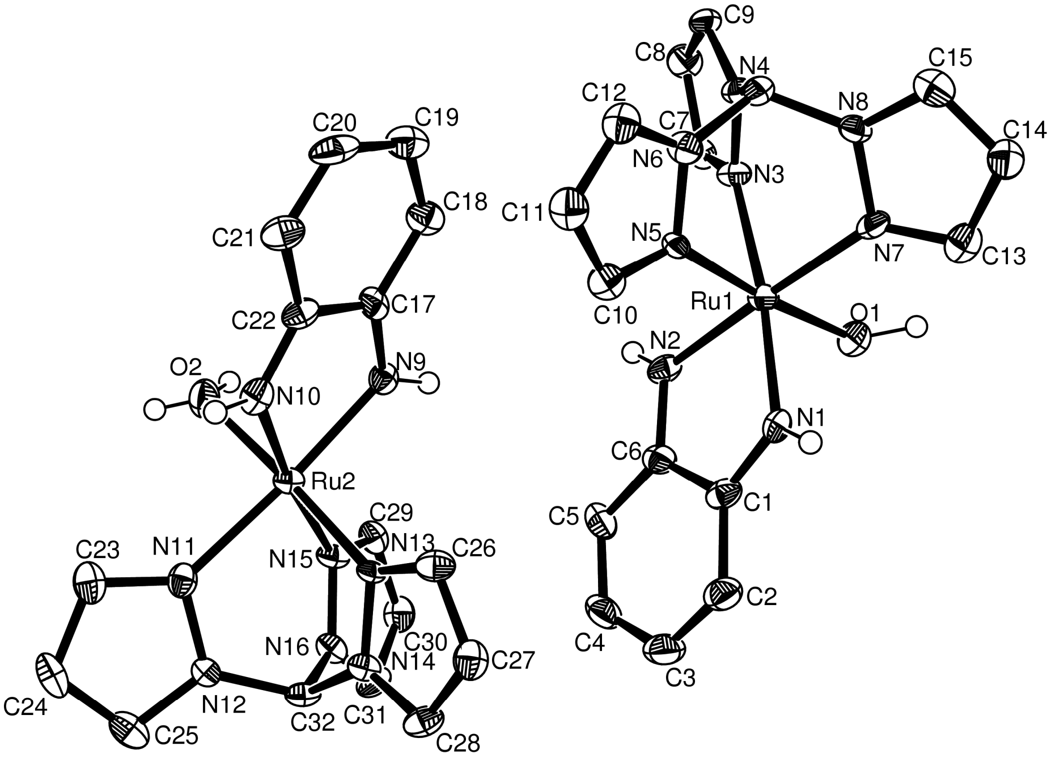
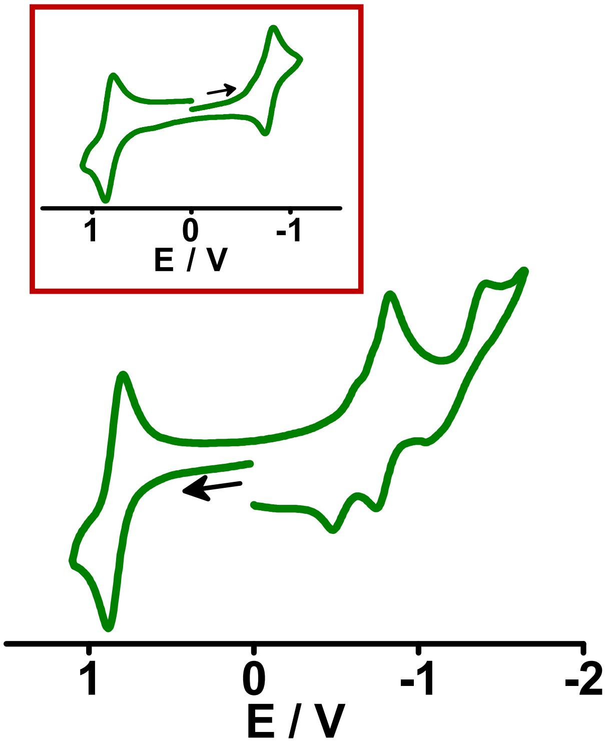
Ru1
N2
N1
Cl1
C6
C1
C5
C2
C4
C3

Fig. 1



Molecule B **Molecule A**

Fig. 2



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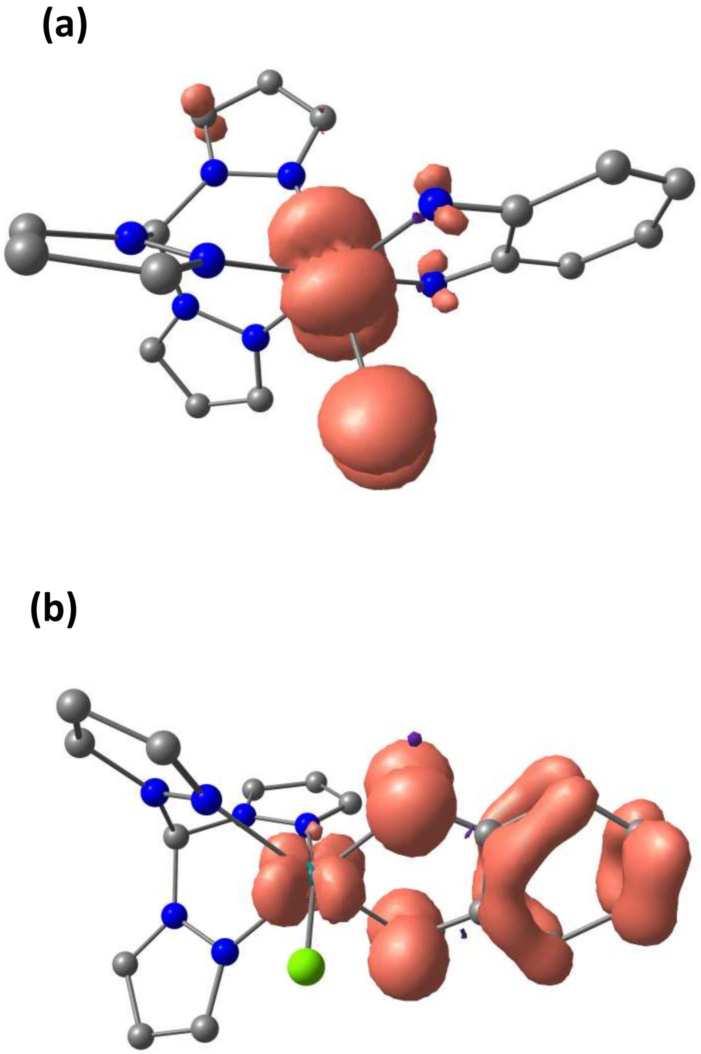

Fig. 4

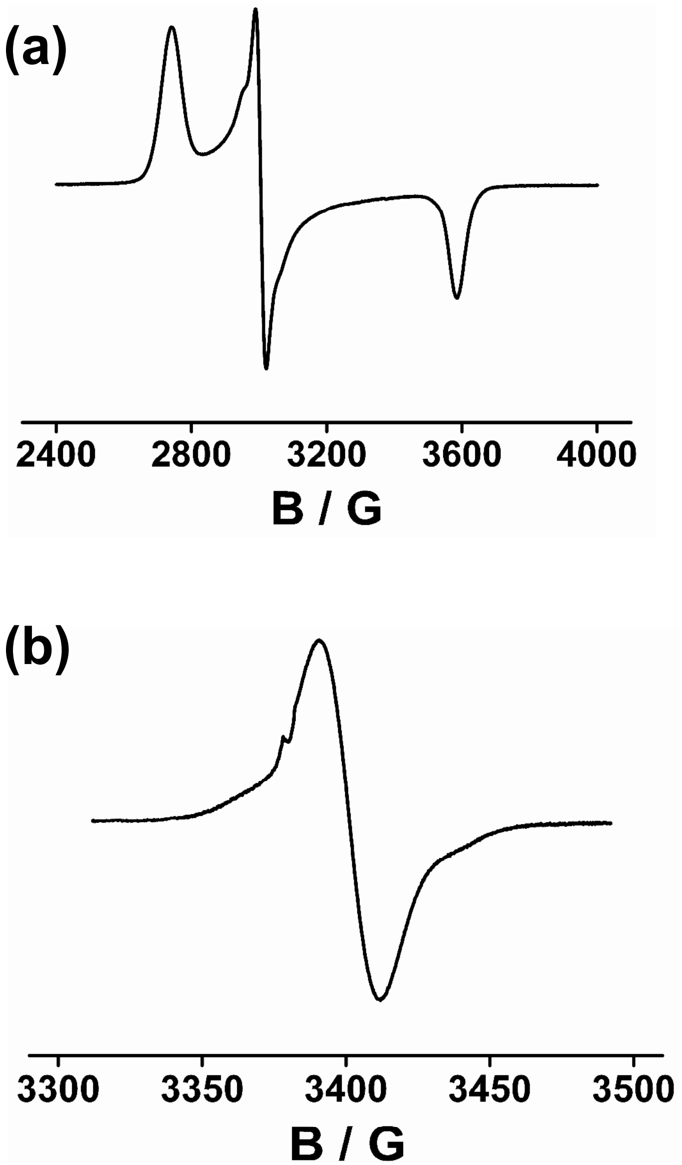

Fig. 5

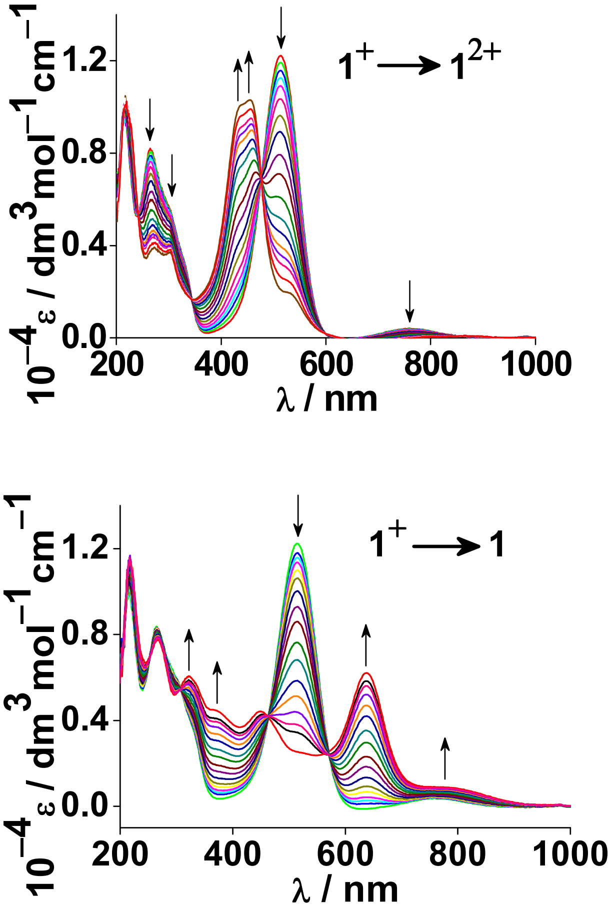
$1^+ \longrightarrow 1^{2+}$
10^{-4} ε / dm^{3}mol^{-1}cm^{-1}
0.0
0.4
0.8
1.2
200
400
600
800
1000
λ / nm
$1^+ \longrightarrow 1$
10^{-4} ε / dm^{3}mol^{-1}cm^{-1}
0.0
0.4
0.8
1.2
200
400
600
800
1000
λ / nm

Fig. 6

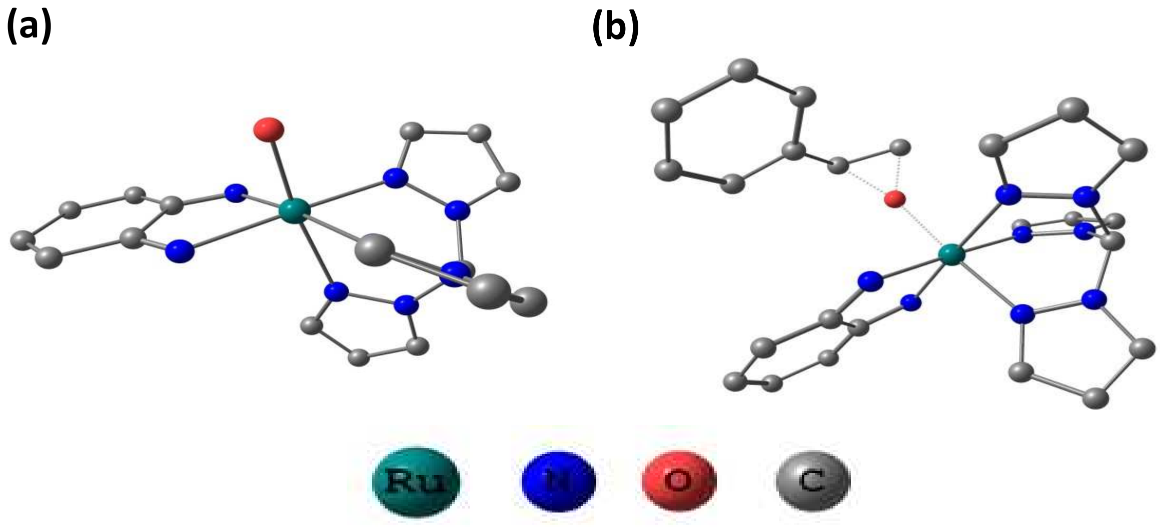

Fig. 7

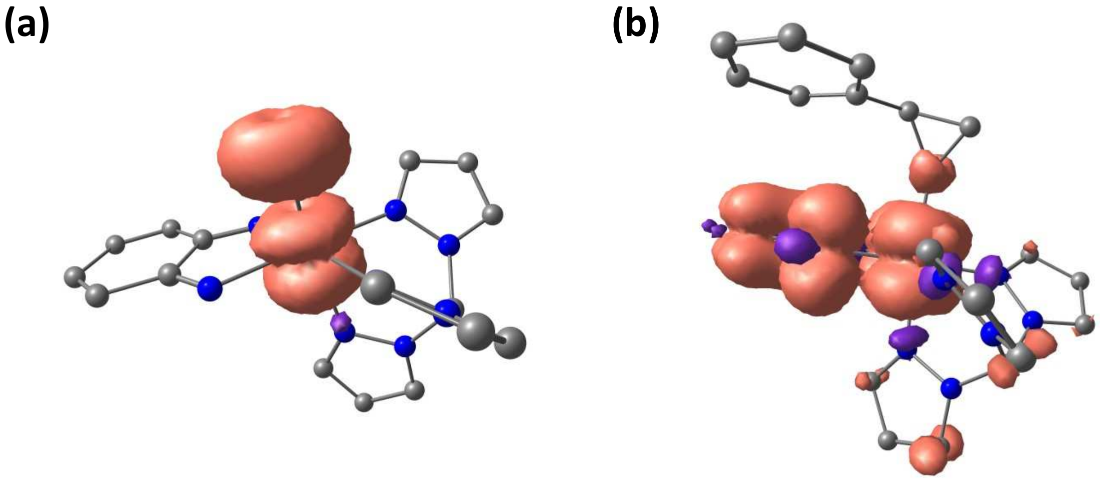

Fig. 8

TOC

Electronic structure and catalytic aspects of [Ru(tpm)(bqdi)(Cl/H$_2$O)]^n, tpm = tris(1-pyrazolyl)methane and bqdi = *o*-benzoquinonediimine

Hemlata Agarwala, Fabian Ehret, Abhishek Dutta Chowdhury, Somnath Maji, Shaikh M. Mobin, Wolfgang Kaim,* and Goutam Kumar Lahiri*

Redox series including $\{Ru^{II}(bqdi^0)Cl/H_2O\}^{n+}$, $\{Ru^{III}(bqdi^0)Cl\}^{2+}$, $\{Ru^{II}(bqdi^{\bullet-})Cl\}^0$, $\{Ru^{III}(bqdi^0)OH\}^{2+}$, $\{Ru^{IV}(bqdi^0)O\}^{2+}$ and the application of the aqua complex for selective epoxidation process are reported.