Characterization of the Excited States of *Distal*- and *Proximal*-[Ru(tpy)(pynp)OH₂]²⁺ in Aqueous Solution Using Time-Resolved Infrared Spectroscopy

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Abstract

The quasi-stable excited states of *distal*- and *proximal*-[Ru(tpy)(pynp)OH₂]²⁺ (tpy = 2,2',6',2"-terpyridine, pynp = 2-(2-pyridyl)-1,8-naphthyridine), which exhibits unique irreversible photoisomerization, were assessed in aqueous solution using time-resolved infrared vibrational spectroscopy and quantum chemical calculations. Transient vibrational spectra from 1300 to 1650 cm⁻¹ were acquired 120 and 2 ps after photoexcitation with a 400 nm pulse for the *distal*- and *proximal*-isomers, respectively. The calculated vibrational spectra assuming the lowest triplet states were in good agreement with the experimentally observed spectra, and the vibrational bands are assigned to normal vibrational modes obtained from calculations. The lifetimes of the excited state were determined to be 9.7 ns and 6.4 ps for the *distal*- and *proximal*-isomers, respectively. Based on these results, we determined various characteristic features of these excited states. Despite the large difference in lifetime, both isomers were assigned to the triplet metal-to-ligand charge transfer (³MLCT) state and there was almost no difference in the positions of the atoms directly coordinated to

the Ru atom. The dissimilarity between the isomers is that the pynp ligands are significantly distorted in the case of the *distal*-isomer while there is hydrogen bonding between the pynp and OH₂ ligands in the *proximal*-isomer. The strong interaction between the low lying ³MLCT state and the ground state presumably causes the very short lifetime and the forbidden photoisomerization of the *proximal*-isomer, whereas photoisomerization occurs via the thermally populated metal centered (³MC) state from the high-lying ³MLCT state in the case of the *distal*-isomer.

1. Introduction

Ruthenium(II) complexes with polypyridyl ligands have been applied to a wide variety of devices, including sensors [1,2], photovoltaic cells [3-5], displays [6,7] and photocatalysts [8,9], due to their unique photophysical and photochemical properties typically involving the photoexcited triplet metal to ligand charge transfer ($^3\text{MLCT}$) state. For this reason, the photophysical and photochemical reactions of these compounds, including photoluminescence [8,10,11], photosubstitution [12-15] and photoisomerization [16-21] processes, have been extensively studied. We recently reported the irreversible and stoichiometric photoisomerization of *distal*-[Ru(tpy)(pynp)OH₂]²⁺ [22] (tpy = 2,2',6',2''-terpyridine, pynp = 2-(2-pyridyl)-1,8-naphthyridine) to *proximal*-[Ru(tpy)(pynp)OH₂]²⁺ [18,23] (Scheme 1), which had not previously been characterized in the case of polypyridyl ruthenium(II) aquo complexes. Although the photoisomerization of *cis*-[Ru(bpy)₂(OH₂)₂]²⁺ (bpy = 2,2'-bipyridine) to the *trans* form in a photostationary state in water has been reported, this *trans* form slowly reverts back to the original *cis* form by a thermal reaction [16].

Scheme 1. Photoisomerization of *distal* to *proximal*-[Ru(tpy)(pynp)OH₂]²⁺

Quantum chemical calculations undertaken to provide mechanistic insight into the photoisomerization of *distal*-[Ru(tpy)(pynp)OH₂]²⁺ to *proximal*-[Ru(tpy)(pynp)OH₂]²⁺ have suggested that the photo-dissociation of an aquo ligand on the *distal*-[Ru(tpy)(pynp)OH₂]²⁺ occurs via the $^3\text{MLCT}$ state to give a penta-coordinated [Ru(tpy)(pynp)]²⁺ intermediate [23]. Based on this, we determined a pathway for conversion from this penta-coordinated [Ru(tpy)(pynp)]²⁺ (*distal*-penta) intermediate, incorporating the structure (bond lengths and angles) of the *distal*-isomer, to a *proximal*-penta intermediate with the dimensions of the *proximal*-isomer. Re-coordination of a water molecule following this conversion produces the *proximal*-isomer [23]. The calculations also suggested that the photo-dissociation of an aquo ligand could be suppressed by intramolecular hydrogen bonding (O-H...N) between a hydrogen on an aquo ligand and an uncoordinated nitrogen on the naphthyridine moiety of the pynp, thereby preventing the *proximal*-isomer from

undergoing reverse photoisomerization to the *distal*-isomer [18,23]. Preliminary nanosecond laser flash photolysis experiments have also been performed to gain a better understanding of the dynamics of the excited states. The resulting UV-visible absorption spectral change allowed the lifetime of the excited $^3\text{MLCT}$ state of the *distal*-[Ru(tpy)(pynp)OH₂]²⁺ isomer to be determined, with a value of 8.9 ns (albeit with the potential for significant error due to the 4 ns pulse duration applied) at 275 K. In contrast, no spectral change was observed for *proximal*-[Ru(tpy)(pynp)OH₂]²⁺ at 275 K, suggesting that the lifetime of the $^3\text{MLCT}$ state of the *proximal*-isomer (at less than 1 ns) is much shorter than that of the *distal*-isomer [23]. Thus, the information available regarding the photoexcited states of the *proximal*- and *distal*-isomers was too limited to reveal the photoisomerization mechanism.

Time-resolved infrared vibrational spectroscopy (TR-IR) is a powerful tool for studying excited states of a molecule because the complex vibrational spectral pattern is very sensitive to local structures and charge distributions in the molecule. Nevertheless, TR-IR is not widely used for studying excited states of metal complexes except for those having a CO or CN group, both of which exhibit strong IR absorption and give isolated vibrational peaks. Previously, we conducted detailed studies of the excited states of prototypical ruthenium(II) complexes having only polypyridyl ligands and assigned the transient vibrational bands in the fingerprint region from 1000 to 1700 cm⁻¹ to normal vibrational modes obtained by quantum chemical calculations [24]. In the present work, we applied the same method to the study of the excited states of *distal*- and *proximal*-[Ru(tpy)(pynp)OH₂]²⁺. One challenge associated with this work was that these complexes had to be assessed in aqueous solution, which exhibits strong IR absorption. We were able to solve this problem by using an infrared cell with a short path length and by employing heavy water, the IR absorption of which is relatively weak within the region being studied. As a result, we were able to successfully acquire TR-IR spectra at 1300 to 1700 cm⁻¹ and also characterized the excited states of these compounds with the help of quantum chemical calculations.

2. Experimental section

2.1. Materials

Distal-[Ru(tpy)(pynp)Cl]Cl, *distal*-[Ru(tpy)(pynp)OH₂](PF₆)₂ and *proximal*-[Ru(tpy)(pynp)OH₂](PF₆)₂ were prepared and characterized according to methods already reported in the literature [23].

2.2. Instrumentation

IR vibrational spectra in the ground state were acquired using a Fourier transform infrared spectrometer (FT-IR, Shimadzu IR Prestige-21). Samples were prepared as KBr pellets incorporating 0.5 mg of the sample in 150 mg of KBr powder.

TR-IR spectra were obtained by the pump-probe method using a femtosecond Ti:sapphire amplifier (Spectra-Physics Spitfire Ace, pulse duration = 120 fs, wavelength = 800 nm, repetition rate = 1 kHz) in a similar manner to that detailed in our previous reports [24, 25]. For measurements less than one nanosecond, the ultraviolet pump pulse (400 nm) was generated by second harmonic generation (SHG) from a portion of the amplifier output, whereas the tunable mid-infrared probe pulse (1000–3700 cm^{-1}) was generated by optical parametric amplification (OPA) and difference frequency generation (DFG) from the other part of the output. The delay time between the pump and probe pulses was obtained by varying their optical pathlengths using a mechanical stage. For measurements spanning more than one nanosecond, the SHG from the output of a Nd:YVO laser (InnoLas Laser SpitLight, pulse duration = 600 ps, wavelength = 1064 nm, repetition rate = 1 kHz) was used as the pump pulse (532 nm) instead of the above pump pulse. The delay time was obtained by a delay generator (Stanford Research Systems DG645) that was synchronously connected to both lasers.

The pump and probe beams were focused on a sample cell using BaF_2 lenses. The energy and diameter of the pump pulse were 40 $\mu\text{J}/\text{pulse}$ and $\sim 220 \mu\text{m}\phi$, respectively. It was confirmed that the peak intensities were linear with respect to the pump energy up to a value of 40 $\mu\text{J}/\text{pulse}$. The sample cell was an infrared flow cell with CaF_2 windows and an optical path length of 0.1 mm. After passing through the sample cell, the probe beam was dispersed by a 19 cm^{-1} polychromator and data were acquired using a 64-channel MCT (mercury cadmium telluride) infrared detector array. The resolution of the system was $\sim 3 \text{ cm}^{-1}$ and wavenumber calibration was carried out using polyethylene terephthalate and polystyrene films. Each sample solution was prepared at a concentration of 1.3 mM in heavy water (D_2O , 99.8 atom% D) and each solution was sparged with argon for over an hour to remove dissolved oxygen. All measurements were carried out at room temperature ($\sim 295 \text{ K}$).

2.3. Quantum chemical calculations

Optimized structures and vibrational frequencies were obtained using the Gaussian 09 package [26] at the DFT level using the mPW1/PW91 functional and the LanL2DZ basis set. Solvation effects were not considered. In these calculations, the experimentally observed ground and meta-stable excited states were considered to represent the lowest singlet (S_0) and triplet (T_1) states [24]. A scaling factor of 0.96 was

used to fit the calculated frequencies to the observed values for all calculated states. During calculations of the excited state, heavy water (OD_2) was used in place of the water ligand (OH_2) in the complexes because it is known that the water ligand is readily replaced by the heavy water in a D_2O solution [18].

3. Results and discussion

3.1. FT-IR spectra and structures of the ground state

The upper spectra in Figs. 1(a) and 2(a) show the FT-IR vibrational spectra of *distal* and *proximal* $[\text{Ru}(\text{tpy})(\text{pynp})\text{OH}_2](\text{PF}_6)_2$, respectively, whereas the lower figures present the corresponding vibrational spectra of the S_0 state obtained from quantum chemical calculations. In the calculated spectra, the colored bars represent the frequencies and IR absorption intensities of each normal vibrational mode, while the solid curves represent the convoluted spectra obtained from these bars using a Gaussian function with a 4 cm^{-1} bandwidth. The color of each bar indicates the ligand on which the vibrations are localized; red, blue and green represent the tpy, pynp and OH_2 (or OD_2) ligands, respectively, while purple represents both the tpy and pynp ligands. In the experimental spectrum of the *distal*-isomer, narrow bands are present at 1326, 1388, 1414, 1447, 1467, 1490, 1506 and 1542 cm^{-1} , along with a broad band at 1582 to 1615 cm^{-1} . The *proximal*-isomer spectrum is very similar, with narrow bands at 1333, 1391, 1419, 1430, 1448, 1469, 1510, 1541 and 1559 cm^{-1} and a broad band at 1594 to 1678 cm^{-1} . Tables 1 and 2 summarize the observed bands and corresponding calculated vibrational modes for the *distal* and *proximal*-isomers, respectively.

Since the observed and calculated spectra were in good agreement with each other, as shown in Figs. 1(a) and 2(a), we may discuss the detailed relationship between the spectral patterns and molecular structures of the *distal* and *proximal*-isomers based on the calculation results. Figure 3 presents the optimized structures of the isomers. Here the top and bottom structures are those viewed from the directions of the pynp and tpy ligands, respectively. In both isomers, the layouts of the pynp and tpy ligand planes are almost the same. Reflecting this similarity, the spectral shapes of these isomers are similar.

In contrast to the tpy and pynp ligands, the structures of the OH_2 ligands of the *distal* and *proximal*-isomers are very different. In the calculated spectrum of the *distal*-isomer, the vibrational modes assigned to the HOH bending vibration are located at 1594 cm^{-1} as a single peak, whereas in the spectrum of the *proximal*-isomer there are three major modes at 1523, 1560 and 1572 cm^{-1} . Considering that the HOH bending mode of isolated water molecules is located at 1595 cm^{-1} [27], this spectral difference

indicates that the OH₂ ligand of the *distal*-isomer is almost isolated, whereas the *proximal*-isomer OH₂ ligands strongly interact with other atoms. In the optimized structures in Fig. 3, the hydrogen atoms of the OH₂ ligand of the *distal*-isomer are isolated, whereas in the *proximal*-isomer the hydrogen of the OH₂ ligand is bonded to a nitrogen atom on the pynp ligand. This hydrogen bond results in the red shift and splitting of the HOH bending mode of the proximal-isomer. These features of the structures are consistent with previously reported calculation results [23, 28].

3.2. TR-IR spectra and structures of the excited state

The upper spectra in Figs. 1(b) and 2(b) show the TR-IR spectra of *distal*- and *proximal*-[Ru(tpy)(pynp)OD₂]²⁺ in D₂O solution following photoexcitation with a 400 nm pulse. The delay times between the pump and probe pulses were 120 ps and 2 ps for the *distal*- and *proximal*-isomers, respectively, based on the respective lifetimes of the excited states, as discussed below. In the same manner as for the FT-IR spectra, the corresponding calculated vibrational spectra of the T₁ state are shown in the lower figures. In the spectrum of the *distal*-isomer in Fig. 1(b), upward bands are evident at 1309, 1371, 1399, 1428, 1446, 1458, 1474, 1507, 1528, 4559, 1588 and 1607 cm⁻¹ and downward bands are seen at 1326, 1390, 1421, 1452, 1465, 1511, 1538 and 1598 cm⁻¹. In the spectrum of the *proximal*-isomer in Fig. 2(b), there are upward bands at 1301, 1379, 1429, 1445, 1464, 1480, 1546 and 1586 cm⁻¹ and downward bands at 1329, 1391, 1424, 1435, 1453, 1472, 1516, 1539, 1554 and 1606 cm⁻¹. Because the TR-IR spectra show absorbance changes after photoexcitation, the upward bands are attributed to transient absorption in the excited state, whereas the downward bands are attributed to absorption decreases (or bleaching) in the ground state. Thus, the position of each bleaching band must agree with that of the corresponding band in the FT-IR spectra unless there is overlap with transient absorption in the excited state. The TR-IR and FT-IR spectra are compared in Figs. 1(c) and 2(c), confirming that almost all the bleaching bands in the TR-IR spectra are in good agreement with the bands in the FT-IR spectra. This occurred even though the TR-IR and FT-IR spectra were recorded under different sample conditions: in D₂O solution and KBr pellets, respectively. Tables 3 and 4 summarize the observed bands and calculated vibrational modes for the *distal*- and *proximal*-isomers, respectively.

In order to assign the transient absorption bands, these bands were compared to the calculated spectra for the T₁ state. Because of the observed correspondence, the states observed by TR-IR are considered to represent the lowest triplet states (T₁) obtained from calculations. In contrast to the FT-IR spectra, the TR-IR spectra of the *distal*- and

proximal isomers do not resemble one another, and the differences in the spectral patterns and molecular structures of these isomers may be discussed based on the results of calculations in the same manner as in the analysis of the FT-IR spectra. From comparison of the calculated spectra of the *distal* and *proximal* isomers, it is evident that the blue (pynp) and red (tpy) bars are somewhat evenly matched in the *distal* spectrum, whereas the blue bars are more frequent and more intense in the *proximal* spectrum. To show this difference more quantitatively, we estimated the sum totals of intensities of the modes assignable to the pynp and tpy ligands separately for the S_0 and T_1 states of the *distal* and *proximal* isomers, and compared these values by setting the total intensity of the tpy ligand for the S_0 state to a value of one for each isomer. It should be noted that these sum totals were obtained for all calculated vibrational modes including those outside the experimental wavenumber range. These calculations determined that the tpy to pynp intensity ratio was changed from 1:0.9 to 1.1:1.8 in conjunction with the S_0 to T_1 transition of the *distal* isomer, whereas this same ratio went from 1:1.9 to 1.8:7.1 in the case of the *proximal* isomer. This result indicates that the IR absorption intensity of the pynp ligands of the *proximal* isomer is much greater than that of the other ligands in the T_1 state, generating the observed differences in the TR-IR spectra of the *distal* and *proximal* isomers.

The observation that a specific ligand (the pynp ligand of the *proximal* isomer) becomes more IR active following photoexcitation implies that the ligand undergoes charge and/or structural changes in the excited state. We first examined the molecular orbitals (MOs) associated with the S_0 and T_1 states of the *distal* and *proximal* isomers shown in Figs. 4 and 5, respectively. We estimated contributions of MOs to the T_1 state based on time-dependent DFT (TD-DFT) calculations using the S_0 optimized structure [24] and found that the major transition is HOMO $\rightarrow$ LUMO for both the isomers, 56.6% for the *distal* and 93.7% for the *proximal* isomers. Since the contribution of HOMO-1 $\rightarrow$ LUMO is significant (37.5%) for the *distal* isomer, HOMO-1 was added in Figs. 4 and 5. In addition, spin density distribution in the T_1 state was shown in Figs. 4 and 5. These MOs clearly show that there are no significant differences between the isomers. For both the isomers, the HOMO of the S_0 state is localized mainly at the central Ru atom and spreads partially over the tpy and pynp ligands. The HOMO-1 is similar but spreads over the pynp ligand somewhat more. On the other hand, the SOMOs and spin density of the T_1 state are localized mostly on the pynp ligands. These variations of the MOs accompanying the S_0 to T_1 transition indicate that the observed excited state corresponds to the $^3\text{MLCT}$ state.

We next considered the structural changes in the excited states and Fig. 6 presents

the optimized structures of the T_1 state obtained from calculations. In the same manner as adopted for the S_0 state in Fig. 3, the top and bottom structures in this figure are viewed from the directions of the pynp and tpy ligands, respectively, and the lighter color atoms represent those in the S_0 state, to more clearly depict the structural changes. A notable structural change is that the pynp ligand of the *distal*-isomer is significantly distorted in the T_1 state, whereas that of the *proximal*-isomer is not so greatly changed. From these charge and structural changes, we may conclude that the pynp ligand becomes IR active on photoexcitation due to the charge localization on the ligand in its excited state, in the case of both the *distal* and *proximal*-isomers. This phenomenon, in which a charge-localized ligand becomes IR active as the result of photoexcitation, has been reported for another ruthenium complex, $[\text{Ru}(\text{bpy})_2(\text{bpm})]^{2+}$ [24]. However, the large structural change of the pynp ligand in the excited state for the *distal*-isomer reduces its IR activity. Considering that the calculated intensities are obtained from the transition dipole moments in the potentials of optimized structures, this reduction of IR activity due to structural distortion is presumably essential.

Because the molecular orbitals and optimized structures obtained by calculations work to explain the experimentally observed vibrational spectra, the calculation results are considered to be reliable. Therefore, we are able to discuss the details of the molecular structures of the excited states for both isomers. Figure 6 also shows the manner in which the major structural parameters are varied by the S_0 to T_1 transition, and two characteristic features are evident from these parameters. Firstly, the dihedral angle of the pynp plane to the tpy plane varies from 180° to 161° as a result of this transition in the case of the *distal*-isomer, whereas the angle does not change in the case of the *proximal*-isomer. Observing the variation of the pynp plane of the *distal*-isomer more closely, it can be seen that the pynp plane is bent at the bond between the naphthyridine and bipyridine rings. This variation of the pynp ligand presumably originates from steric hindrance due to the charge localization on the pynp ligand in the T_1 state. That is, the extended π^* -orbital of the pynp ligand sterically hinders the π -orbital of the tpy ligand and the pynp plane is bent to avoid this hindrance. This speculation is supported by the fact that the bipyridine-ring of the pynp is located at the position at which the π -electron density is lowest, representing the σ -bond between the pyridine rings of the tpy ligand.

The second observation that can be made relates to the coordination structure of the OH_2 ligand. For the *proximal*-isomer, the bond length between the central metal and the oxygen atom of the ligand is slightly reduced, from 2.21 to 1.98 Å, by the S_0 to T_1 transition, while the hydrogen bond between the pynp ligand and the OH_2 ligand is

significantly reduced, from 1.48 to 1.06 Å. In contrast, there are no changes in the bond lengths induced in the *distal*-isomer by the transition. The significant reduction of the hydrogen bond length presumably results from the same cause as the angle variations discussed above. In the *proximal*-isomer, the extended π^* -orbital of the pynp ligand in the T_1 state interacts more strongly with the OH_2 than with the π -orbital in the S_0 state, whereas there is no such hydrogen bond in the *distal*-isomer.

3.3. Lifetimes and dynamic processes of the excited states

In order to obtain information regarding the dynamics of the excited states, we measured the temporal variations of the observed vibrational bands. Figures 7(a) and (b) show the temporal profiles of the peak intensities of the bands at 1309 cm^{-1} for the *distal*-isomer and at 1301 cm^{-1} for the *proximal*-isomer, respectively. The band shapes were observed not to vary with the delay times. By fitting using a single exponential function, we obtained a three order of magnitude difference in the lifetimes of 9.7 ns and 6.4 ps for the *distal*- and *proximal*-isomers, respectively. These lifetimes did not depend on the vibrational bands, indicating that all the observed vibrational bands may be assigned to the same excited state.

In general, 3MLCT states of Ru polypyridyl complexes exhibit long lifetimes, in the nanosecond range or above, because the transition from a triplet excited state to a singlet ground state is forbidden. Thus, the 6.4 ps lifetime observed in the case of the *proximal*-isomer is extraordinarily short and indicates the formation of a state that strongly interacts with the 3MLCT state and accelerates a non-radiative process. One of the most well-known such states is the metal centered state (MC), attributed to splitting of the d-orbitals of the central metal by the ligand field [29]. As an example, the lifetime of the 3MLCT state of $[Ru(bpy)_3]^{2+}$ is determined by the non-radiative relaxation that occurs via the thermally populated 3MC state located approximately 3500 cm^{-1} above the 3MLCT state [30]. Consequently, we may qualitatively estimate the energy positions of the 3MC states of the *distal*- and *proximal*-isomers based on ligand field theory. To assist in assessing the coordination structures of the complexes, the positions of the atoms that are directly coordinated to the Ru atom and the atomic distances between these atoms and Ru are summarized in Fig. 8.

Based on the ligand field theory for a six-coordinate Ru complex, the energy splitting between the t_{2g} (d_{xy} , d_{xz} , d_{yz}) and e_g (d_{z^2} , $d_{x^2-y^2}$) orbitals will be determined by the coordination structure. As an example, a closer placement of the ligand corresponds to a larger energy splitting between the t_2 and e_g orbitals. Consequently, the MC state is located at higher energy. If the 3MC state is at a higher energy, the lifetime of the

$^3\text{MLCT}$ state will be increased because the thermal population of the ^3MC state, which leads to non-radiative decay, is reduced. Figure 8 shows that there is almost no difference in the coordination structures of the N atoms between the *distal* and *proximal*-isomers and that there is only a slight difference in the positions of the O atoms. The distance between the Ru and O atoms in the *proximal*-isomer is slightly shorter than in the *distal*-isomer, indicating that the d-orbitals splitting energy for the *proximal*-isomer is almost the same as or somewhat larger than that for the *distal*-isomer. Thus, the position of the ^3MC state cannot be the cause of the three order of magnitude difference in the lifetime between the two isomers.

We may also consider the possibility that the large difference in the $^3\text{MLCT}$ state energies of the *distal* and *proximal*-isomers results in differences in their respective decay processes via states other than a ^3MC state. The calculated difference in the energies of the S_0 and T_1 states are $15 \times 10^3 \text{ cm}^{-1}$ for the *distal*-isomer and $8.5 \times 10^3 \text{ cm}^{-1}$ for the *proximal*-isomer. This difference between the isomers likely originates from the large distortion of the pynp ligand in the case of the *distal*-isomer. Figure 9 illustrates the energy levels of these states together with those of the other important states. In this model, the non-radiative decay of the *distal*-isomer takes place via the thermally populated ^3MC state, as supported by the previously reported observation that the decay rate depends on temperature [23]. In contrast, the very quick decay (6.4 ps lifetime) for the *proximal*-isomer indicates that the associated decay process is non-thermal. Considering that the $^3\text{MLCT}$ state of the *proximal*-isomer exists at much lower energies than that of *distal*-isomer, the ^3MC state is located at much higher energies than the $^3\text{MLCT}$ state, and that the structure of the $^3\text{MLCT}$ state resembles the S_0 state, we conclude that the rapid decay of the $^3\text{MLCT}$ state is caused by direct relaxation to the ground state due to the strong interaction between the $^3\text{MLCT}$ and ground states.

Non-radiative decay rates from an excited state to a ground state in metal complexes are often discussed based on the energy-gap law: the rate decreases exponentially with increasing energy gap [31-34]. Concerning the *proximal*-isomer, the structure geometries of the S_0 and T_1 states are almost the same; thus, the law can be applied as the weak coupling limit. The difference in energy between the T_1 and S_0 states was estimated to be $8.5 \times 10^3 \text{ cm}^{-1}$. Because this energy gap is much smaller than those of general metal complexes shown in the literature, $13 - 19 \times 10^3 \text{ cm}^{-1}$, the energy gap law can explain the short lifetime at least qualitatively. In contrast, the large difference in structure between the S_0 and T_1 states of the *distal*-isomer prevents us from applying the energy gap law simply because it is difficult to estimate the Franck-Condon factor.

In addition, there is another possibility that the hydrogen bonding existing only in the *proximal*-isomer facilitates the non-radiative decay through its low-frequency vibrations.

A change in isomerization from the *distal* to *proximal*-isomers was not directly observed by TR-IR spectroscopy, likely because the associated quantum yield of 1.5% [18] is not large enough to be detected by our instrumentation. However, the TR-IR data are sufficient to demonstrate that the lifetime of the excited state of the *proximal*-isomer is too short to allow it to undergo the thermal isomerization reaction like the *distal*-isomer. It is also reasonably certain that the long lifetime and distorted structure of the $^3\text{MLCT}$ state of the *distal*-isomer leads to isomerization via thermal excitation.

4. Conclusion

We successfully acquired transient vibrational spectra of quasi-stable excited states of *distal*- and *proximal*-[Ru(tpy)(pynp)OH₂]²⁺ in water within the fingerprint region of 1300 to 1650 cm⁻¹, using TR-IR spectroscopy with a femtosecond Ti:sapphire amplifier and a multi-channel infrared detector array. The results of quantum chemical calculations at the DFT level are in good agreement with the observed spectra obtained 120 and 2 ps after photoexcitation by a 400 nm pulse for the *distal* and *proximal*-isomers, respectively, indicating that the calculated optimized structures well reproduce the excited structures at these delay times. We also found that there is a three order of magnitude difference in the lifetimes of the excited states of the isomers (9.7 ns for the *distal* and 6.4 ps for the *proximal*) based on the temporal profiles of the vibrational bands. These experimental and theoretical results revealed the characteristic features of the photoexcited states and the photoisomerization processes that occur via these states. Molecular orbital calculations indicated that the excited states of both isomers are assigned to the $^3\text{MLCT}$ state. The positions of the atoms directly coordinated to the Ru atom are very similar to one another, showing that there is little difference in the energy values of the ^3MC states between the isomers. In contrast, there is a large difference in terms of the structures of the pynp ligands and the hydrogen bonding of the OH₂ ligands. The pynp ligand is distorted in the excited state of the *distal*-isomer whereas the OH₂ ligand is hydrogen bonded to one of the nitrogen atom of the pynp ligand for the *proximal*-isomer. This difference generates significant variation in the energies of the $^3\text{MLCT}$ states and induces different photoexcited dynamics in the two isomers; the high-lying $^3\text{MLCT}$ state of the *distal*-isomer undergoes photoisomerization via the thermally populated ^3MC state

whereas the low-lying state of the *proximal*-isomer leads a quick relaxation by direct interaction with the ground state. The results also show that the combination of TR-IR spectroscopy and DFT calculations is a powerful tool for the characterization of the excited state and elucidation of photoexcited dynamics in metal complexes in aqueous solutions, even without the presence of characteristic ligands such as CO and CN.

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References

- [1] P. Anzenbacher, D.S. Tyson, K. Jursíková, F.N. Castellano, Luminescence lifetime-based sensor for cyanide and related anions, *J. Am. Chem. Soc.*, 124 (2002) 6232-6233.
- [2] M. Montalti, S. Wadhwa, W.Y. Kim, R.A. Kipp, R.H. Schmehl, Luminescent ruthenium(II) bipyridyl-phosphonic Acid complexes: pH dependent photophysical behavior and quenching with divalent metal ions, *Inorg. Chem.*, 39 (1999) 76-84.
- [3] B. O'Regan, M. Gratzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films, *Nature*, 353 (1991) 737-740.
- [4] K. Kalyanasundaram, M. Grätzel, Applications of functionalized transition metal complexes in photonic and optoelectronic devices, *Coord. Chem. Rev.*, 177 (1998) 347-414.
- [5] P. Wang, S.M., Zakeeruddin, J.E. Moser, M.K. Nazeeruddin, T. Sekiguchi, M. Gratzel, A stable quasi-solid-state dye-sensitized solar cell with an amphiphilic ruthenium sensitizer and polymer gel electrolyte, *Nat Mater*, 2 (2003) 402-407.
- [6] F.G. Gao, A.J. Bard, Solid-state organic light-emitting diodes based on tris(2,2'-bipyridine)ruthenium(II) Complexes, *J. Am. Chem. Soc.*, 122 (2000) 7426-7427.
- [7] M. Buda, G. Kalyuzhny, A.J. Bard, Thin-film solid-state electroluminescent devices based on tris(2,2'-bipyridine)ruthenium(II) complexes, *J. Am. Chem. Soc.*, 124 (2002) 6090-6098.
- [8] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Von Zelewsky, Ru(II) polypyridine complexes - photophysics, photochemistry, electrochemistry, and

- chemi-luminescence, *Coord. Chem. Rev.*, 84 (1988) 85-277.
- [9] M. Kirch, J.-M. Lehn, J.-P. Sauvage, Hydrogen generation by visible light irradiation of aqueous solutions of metal complexes. An approach to the photochemical conversion and storage of solar energy, *Helv. Chim. Acta*, 62 (1979) 1345-1384.
- [10] K. Kalyanasundaram, Photophysics, photochemistry and solar energy conversion with tris(bipyridyl)ruthenium(II) and its analogues, *Coord. Chem. Rev.*, 46 (1982) 159-244.
- [11] V. Balzani, A. Juris, Photochemistry and photophysics of Ru(II)-polypyridine complexes in the Bologna group. From early studies to recent developments, *Coord. Chem. Rev.*, 211 (2001) 97-115.
- [12] D.V. Pinnick, B. Durham, Photosubstitution reactions of $\text{Ru}(\text{bpy})_2\text{XY}^{n+}$ complexes, *Inorg. Chem.*, 23 (1984) 1440-1445.
- [13] B. Durham, J.L. Walsh, C.L. Carter, T.J. Meyer, Synthetic applications of photosubstitution reactions of poly(pyridyl) complexes of ruthenium(II), *Inorg. Chem.*, 19 (1980) 860-865.
- [14] C.R. Hecker, P.E. Fanwick, D.R. McMillin, Evidence for dissociative photosubstitution reactions of $[\text{Ru}(\text{trpy})(\text{bpy})(\text{NCCH}_3)]^{2+}$ - crystal and molecular structure of $[\text{Ru}(\text{trpy})(\text{bpy})(\text{py})](\text{PF}_6)_2 \cdot (\text{CH}_3)_2\text{CO}$, *Inorg. Chem.*, 30 (1991) 659-666.
- [15] B.S. Howerton, D.K. Heidary, E.C. Glazer, Strained ruthenium complexes are potent light-activated anticancer agents, *J. Am. Chem. Soc.*, 134 (2012) 8324-8327.
- [16] B. Durham, S.R. Wilson, D.J. Hodgson, T.J. Meyer, Cis-trans photoisomerization in $[\text{Ru}(\text{bpy})_2(\text{OH}_2)_2]^{2+}$ - crystal structure of trans- $[\text{Ru}(\text{bpy})_2(\text{OH}_2)(\text{OH})](\text{ClO}_4)_2$, *J. Am. Chem. Soc.*, 102 (1980) 600-607.
- [17] G.B. Porter, R.H. Sparks, Photoracemization of $\text{Ru}(\text{bipyridine})_3^{2+}$, *J. Photochem.*, 13 (1980) 123-131.
- [18] H. Yamazaki, T. Hakamata, M. Komi, M. Yagi, Stoichiometric photoisomerization of mononuclear ruthenium(II) monoaquo complexes controlling redox properties and water oxidation catalysis, *J. Am. Chem. Soc.*, 133 (2011) 8846-8849.
- [19] S.K. Padhi, R. Fukuda, M. Ehara, K. Tanaka, Photoisomerization and proton-coupled electron transfer (PCET) promoted water oxidation by mononuclear cyclometalated ruthenium catalysts, *Inorg. Chem.*, 51 (2012) 5386-5392.
- [20] A.A. Rachford, J.J. Rack, Picosecond isomerization in photochromic ruthenium-dimethyl sulfoxide complexes, *J. Am. Chem. Soc.*, 128 (2006) 14318-14324.
- [21] S. Miyazaki, T. Kojima, S. Fukuzumi, Photochemical and thermal isomerization of a ruthenium(II)-alloxazine complex involving an unusual coordination mode, *J. Am. Chem. Soc.*, 130 (2008) 1556-1557.

- [22] The *proximal* and *distal* isomers were defined by the structural configuration between a naphthyridine moiety of the pynp ligand and an aquo ligand.
- [23] M. Hirahara, M.Z. Ertem, M. Komi, H. Yamazaki, C.J. Cramer, M. Yagi, Mechanisms of photoisomerization and water-oxidation catalysis of mononuclear ruthenium(II) monoaquo complexes, *Inorg. Chem.*, 52 (2013) 6354-6364.
- [24] T. Mukuta, N. Fukazawa, K. Murata, A. Inagaki, M. Akita, S. Tanaka, S. Koshihara, K. Onda, Infrared vibrational spectroscopy of $[\text{Ru}(\text{bpy})_2(\text{bpm})]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ in the excited triplet state, *Inorg. Chem.* 53 (2014) 2481-2490.
- [25] S. Sato, Y. Matubara, K. Koike, M. Falkenström, T. Katayama, Y. Ishibashi, H. Miyasaka, S. Taniguchi, H. Chosrowjan, N. Mataga, N. Fukazawa, S. Koshihara, K. Onda, O. Ishitani, Photochemistry of *fac*- $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$, *Chem. Eur. J.* 18 (2012) 15722-15734.
- [26] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J. E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J. B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, revision A.2.; Gaussian, Inc.: Wallingford, CT, 2009.
- [27] G. Herzberg, *Molecular Spectra and Molecular Structure* vol. III, reprint edition (Krieger Publishing Co. Malabar, Florida, 1991).
- [28] L. Ding, L.W. Chung, K. Morokuma, Excited-state proton transfer controls irreversibility of photoisomerization in mononuclear ruthenium(II) monoaquo complexes: a DFT study, *J. Chem. Theory Comput.* 10 (2014) 668-675.
- [29] D. W. Thompson, A. Ito, T. J. Meyer, $[\text{Ru}(\text{bpy})_3]^{2+*}$ and other remarkable metal-to-ligand charge transfer (MLCT) excited states, *Pure Appl. Chem.* 85 (2003) 1257-1305.
- [30] J. Van Houten, R. J. Watts, Temperature dependence of the photophysical and photochemical properties of the tris(2,2'-bipyridyl)ruthenium(II) ion in aqueous solution, *J. Am. Chem. Soc.* 98 (1976) 4853-4858.
- [31] J. V. Caspar, E. M. Kober, B. P. Sullivan, T. J. Meyer, Application of the energy gap

law to the decay of charge-transfer excited states, J. Am. Chem. Soc. 104 (1982) 630-632.

[32] J. V. Caspar, B. P. Sullivan, E. M. Kober, T. J. Meyer, Application of the energy gap law to the decay of charge-transfer excited states, solvent effects, Chem. Phys. Lett. 91 (1982) 91-95.

[33] J. V. Caspar, T. J. Meyer, Application of the energy gap law to nonradioactive, excited-state decay, J. Phys. Chem. 87 (1983) 952-957.

[34] E. M. Kober, J. V. Caspar, R. S. Lumpkin, T. J. Meyer, Application of the energy gap law to excited-state decay of Osmium(II)-Polypyridine complexes: calculation of relative nonradiative decay rates from emission spectral profiles, J. Phys. Chem. 90 (1986) 3722-3734.

Figure Captions

Figure 1. Infrared vibrational spectra of *distal*-[Ru(tpy)(pynp)OH₂]²⁺: (a) experimental FT-IR spectrum in the ground state (upper) and calculated spectrum for the S₀ state (lower) of the PF₆ salt, (b) experimental TR-IR spectrum 120 ps after photoexcitation with a 400 nm pulse (upper) and calculated spectrum for the T₁ state (lower) of a D₂O solution (bars in both calculated spectra indicate the wavenumbers and intensities of each vibrational mode and their colors represent the ligand on which the vibrations are localized as listed in Tables 1 and 2), (c) comparison between the TR-IR and FT-IR spectra.

Table 1. Observed vibrational bands in the FT-IR spectrum of *distal*-[Ru(tpy)(pynp)OH₂]²⁺ and corresponding calculated vibrational modes for the S₀ state.

Table 2. Observed vibrational bands in the FT-IR spectrum of *proximal*-[Ru(tpy)(pynp)OH₂]²⁺ and corresponding calculated vibrational modes for the S₀ state.

Figure 2. Infrared vibrational spectra of *proximal*-[Ru(tpy)(pynp)OD₂]²⁺: (a) experimental FT-IR spectrum in the ground state (upper) and calculated spectrum for the S₀ state (lower) of the PF₆ salt, (b) experimental TR-IR spectrum 2 ps after photoexcitation with a 400 nm pulse (upper) and calculated spectrum for the T₁ state (lower) of a D₂O solution (bars in both calculated spectra indicate the wavenumbers and intensities of each vibrational mode and their colors represent the ligand on which the vibrations are localized as listed in Tables 3 and 4), (c) comparison between the TR-IR and FT-IR spectra.

Table 3. Observed vibrational bands in the TR-IR spectrum of *distal*-[Ru(tpy)(pynp)OH₂]²⁺ and corresponding calculated vibrational modes of the T₁ state.

Table 4. Observed vibrational bands in the TR-IR spectrum of *proximal*-[Ru(tpy)(pynp)OH₂]²⁺ and corresponding calculated vibrational modes of the T₁ state.

Figure 3. Optimized structures obtained by quantum chemical calculations of the S₀

states of *distal* and *proximal*[Ru(tpy)(pynp)OH₂]²⁺ together with characteristic structural parameters. The top and bottom structures are viewed from the directions of the pynp and tpy ligands, respectively.

Figure 4. Molecular orbitals of the S₀ state for *distal*[Ru(tpy)(pynp)OH₂]²⁺ (upper) and molecular orbitals and spin density distribution of the T₁ state for *distal*[Ru(tpy)(pynp)OD₂]²⁺ (lower). Inset shows contributions of molecular orbitals to the T₁ state based on TD-DFT calculations.

Figure 5. Molecular orbitals of the S₀ state for *proximal*[Ru(tpy)(pynp)OH₂]²⁺ (upper) and molecular orbitals and spin density distribution of the T₁ state for *proximal*[Ru(tpy)(pynp)OD₂]²⁺ (lower). Inset shows contributions of molecular orbitals to the T₁ state based on TD-DFT calculations.

Figure 6. Optimized structures obtained by quantum chemical calculations for the T₁ states of *distal* and *proximal*[Ru(tpy)(pynp)OD₂]²⁺ together with characteristic variations of structural parameters accompanying the S₀ to T₁ transition. Lighter color atoms represent the S₀ state structure and the top and bottom structures are viewed from the directions of the pynp and tpy ligands, respectively.

Figure 7. Temporal profiles of the peak intensities of vibrational bands (black circles and line) and fitting curves using an exponential function (red line); (a) bands at 1309 cm⁻¹ for *distal*[Ru(tpy)(pynp)OD₂]²⁺ and (b) bands at 1301 cm⁻¹ for *proximal*[Ru(tpy)(pynp)OD₂]²⁺.

Figure 8. The positions and atomic distances of the atoms directly coordinated to the Ru atom as obtained from the optimized structures of the T₁ states of *distal* and *proximal*[Ru(tpy)(pynp)OD₂]²⁺.

Figure 9. Schematic diagram depicting the expected energies of the states of *distal* and *proximal*[Ru(tpy)(pynp)OD₂]²⁺. The numerical values represent the energy differences estimated from calculations.

Fig. 1. S. Tanaka et al.

Table 1. S. Tanaka

FT-IR (S_0 state)			
<i>distal</i> -[Ru(tpy)(pynp)OH ₂](PF ₆)			
Obs.	Calc.*	Assignment	
		Vibration mode	Ligand type
	1178	N=C=N asym. stretching	pynp
	1230	N=C stretching	pynp
	1234	N=C stretching	tpy
	1264	C=N=C asym. stretching	pynp
1326	1282	C-C bridge stretching	pynp
	1292	C-C bridge bending	pynp
1388	1333	C=N=C sym. stretching	tpy
1414	1358	C=N=C sym. stretching	pynp
	1368	C=N=C asym. stretching	pynp
	1374	C=C asym. stretching	tpy
1447	1389	C=C asym. stretching	tpy
1467	1417	C=C asym. stretching	pynp
1490	1493	C-C asym. bridge stretching	tpy
1506	1511	C=C asym. stretching	pynp
1542	1539	C=C=C sym. stretching	pynp
1582 - 1615	1594	OH bending	H ₂ O
1582 - 1615	1599	C=C stretching	pynp
1582 - 1615	1604	C=C stretching(pynp), C=C stretching(tpy) and OH bending	all
1582 - 1615	1605	C=C stretching(pynp), C=C stretching(tpy) and OH bending	all
1582 - 1615	1606	C=C asym. stretching	tpy
1582 - 1615	1608	C=C sym. stretching	tpy
1582 - 1615	1614	C=C stretching	pynp

*Scaling factor = 0.960

Table 2. S. Tanaka

FT-IR (S_0 state)			
<i>proximal</i> -[Ru(tpy)(pynp)OH ₂](PF ₆)			
Obs.	Calc.*	Assignment	
		Vibration mode	Ligand type
	1233	N=C=N asym. stretching	pynp
	1279	N=C stretching	pynp
1333	1330	C-C bridge stretching	pynp
	1336	C-C bridge bending	pynp
1391	1380	C=N=C sym. stretching	tpy
1419	1415	C=N=C stretching	pynp
	1420	C=C=C stretching	pynp
1430	1426	C=N=C asym. stretching	tpy
1448	1441	C=C asym. stretching	tpy
1469	1465	C=C stretching	tpy and pynp
	1468	C=C sym. stretching	tpy and pynp
	1515	C=C=C asym. stretching	pynp
1510	1523	C=C stretching(pynp) and OH bending	pynp and H ₂ O
1541	1560	C=N=C stretching(pynp) and OH bending	pynp and H ₂ O
1559	1571	C=N=C stretching(pynp), C=C=C stretching(tpy) and OH bending	all
	1572	C=N=C asym. stretching(tpy) and OH bending	tpy and H ₂ O
1594 - 1678	1600	C=C stretching	pynp
1594 - 1678	1604	C=C stretching	pynp
1594 - 1678	1606	C=C asym. stretching	tpy
1594 - 1678	1609	C=C sym. stretching	tpy
1594 - 1678	1613	C=C=C stretching	pynp

*Scaling factor = 0.960

Fig. 2. S. Tanaka et al.

Table 3. S. Tanaka

TR-IR (T_1 state)			
<i>distal</i> -[Ru(tpy)(pynp)OD ₂] ²⁺			
Obs.	Calc.	Assignment	
		Vibration mode	Ligand type
	1232	C=N=C sym. stretching	pynp
	1247	C=C=N stretching	pynp
	1278	C=N=C stretching	pynp
	1286	N=C sym. stretching	tpy
1309	1308	C=N=C asym. stretching	tpy
	1337	C=N=C asym. stretching	tpy
1371	1387	C=N=C asym. stretching	tpy
1399	1398	C=N=C asym. stretching	pynp
	1425	N=C stretching	pynp
1428	1428	N=C asym. stretching	tpy
	1442	C=N=C sym. stretching	tpy
1446	1443	C=C asym. stretching	tpy
	1446	C=C=C asym. stretching	pynp
1458	1458	C=C stretching	pynp
1474	1471	C=C stretching(pynp) and C=C Sym. Stretching(tpy)	tpy and pynp
1507	1505	C=C=C asym. stretching	pynp
1528	1533	C=C=C asym. stretching	pynp
1559	1553	C=C=C asym. stretching	pynp
	1576	C=N=C asym. stretching	tpy
1588	1586	C=C=C asym. stretching	pynp
	1602	C=C sym. stretching	tpy
1607	1605	C=C sym. stretching	tpy
	1608	C=C sym. stretching	tpy

*Scaling factor = 0.960

Table 4. S. Tanaka

TR-IR (T_1 state)			
<i>proximal</i> -[Ru(tpy)(pynp)OD ₂] ²⁺			
Obs.	Calc.	Assignment	
		Vibration mode	Ligand type
1301	1231	C=C stretching	pynp
	1249	N=C stretching	pynp
	1288	C=N=C asym. stretching	tpy
	1307	C=N=C asym. stretching	pynp
	1311	C=N=C sym. stretching	pynp
	1311	C=N=C asym. stretching	tpy
	1324	C=N=C asym. stretching	pynp
	1334	C=N=C asym. stretching	tpy
1379	1375	N=C=N sym. stretching	pynp
	1384	C=N=C asym. stretching(pynp) and C=N=C sym. stretching(tpy)	tpy and pynp
	1386	C=N=C asym. stretching(pynp) and C=N=C sym. stretching(tpy)	tpy and pynp
1429	1426	C-C bridge bending	pynp
	1428	C=N=C sym. stretching	tpy
1445	1439	C-C bridge stretching	pynp
	1443	C=N=C sym. stretching	tpy
	1443	C=C asym. stretching	tpy
1464	1465	C-C bridge stretching	pynp
	1472	C-C sym. bridge stretching	tpy
1480	1480	N=C=N asym. stretching	pynp
1546	1541	C=C=C asym. stretching	pynp
	1563	C=C=C asym. stretching	tpy
	1574	C=C=C asym. stretching	tpy
1586	1582	C=C stretching	pynp
	1599	C=C=C asym. stretching	pynp
	1602	C=C sym. stretching	tpy
	1605	C=C asym. stretching	tpy
	1607	C=C sym. stretching	tpy

*Scaling factor = 0.960

distal

proximal

Fig. 3. S. Tanaka et al.

Fig. 4. S. Tanaka et al.

proximal

S_0 state

T_1 State		
major contribution		%
HOMO	→ LUMO	93.7
HOMO-1	→ LUMO	6.3

T_1 state

Fig. 5. S. Tanaka et al.

Fig. 6. S. Tanaka et al.

Fig. 7. S. Tanaka et al.

distal

proximal

atomic distance

distal-[Ru(tpy)(pynp)OD₂]²⁺

proximal-[Ru(tpy)(pynp)OD₂]²⁺

S₀

T₁

S₀

T₁

Ru - N1	2.09 Å	2.10 Å
Ru - N2	1.99 Å	1.99 Å
Ru - N3	2.09 Å	2.07 Å
Ru - N4	2.07 Å	2.08 Å
Ru - N5	2.07 Å	1.98 Å
Ru - O6	2.18 Å	2.18 Å

2.08 Å	2.09 Å
1.98 Å	1.99 Å
2.09 Å	2.09 Å
2.10 Å	2.11 Å
2.03 Å	2.07 Å
2.12 Å	1.98 Å

Fig. 8. S. Tanaka et al.

Fig. 9. S. Tanaka et al.