

## 外国語要旨

学位論文題目 Theoretical study on excited-state properties of photofunctional molecules

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Molecules are electronically excited by light. The electronic structure of the excited state usually differs from that of the ground state, leading to a variety of chemical phenomena via the electronic excited state. In this background, exerting a function with light attracts one's attention more and more. To elucidate the molecular mechanism of light-induced functions, such as excited-state properties and effects of the molecular environment on them, theoretical study should provide valuable insight. In this thesis, the excited-state properties and the environmental effects for two kinds of photofunctional molecules, 3'-hydroxyechinenone (3'-hECN) and  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  (bpy = 2,2'-bipyridine, dppz = dipyrido[3,3-a:2',3'-c]phenazine) (Figure 1), were discussed from theoretical viewpoints. The former molecule, 3'-hECN, is a chromophore of Orange Carotenoid Protein (OCP), and the latter molecule,  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$ , works as a DNA intercalator.

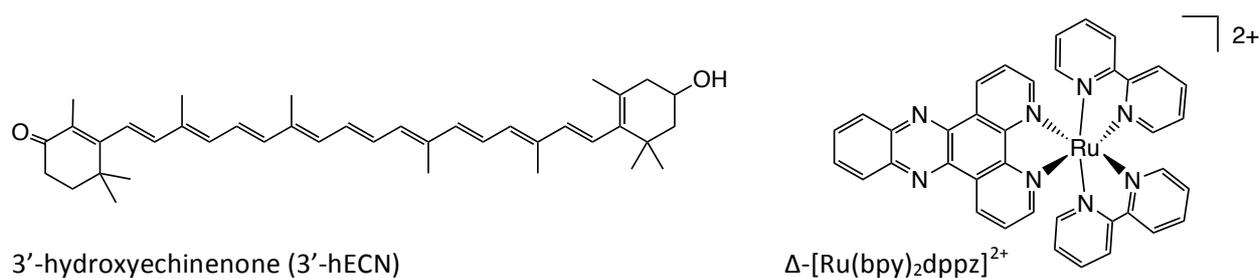


Figure 1. Chemical structural formula of 3'-hECN (left) and  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  (right)

In chapter 1, photophysical processes of electronically excited states and the photo-induced functions of 3'-hECN and  $[\text{Ru}(\text{bpy})_2\text{dppz}]^{2+}$  were overviewed. Previous experimental studies and theoretical studies for those excited-state properties were also described.

In chapter 2, calculation results at TD-DFT and MS-RASPT2 levels for 3'-hECN and the model systems were discussed. It was revealed from TD-DFT calculation that the  $S_0(1^1A_g^-) \rightarrow S_2(1^1B_u^+)$  transition energy is red-shifted by hydrogen bonds with the phenol and indole which is formed in the OCP. Thus, the hydrogen-bonding effect should cause red shift of absorption peak. The  $S_1$  and  $S_2$  states were characterized as the  $2^1A_g^-$  and  $1^1B_u^+$  states, respectively, by the MS-RASPT2 calculation. The  $1^1B_u^+$  state has larger dipole moment compared to the  $1^1A_g^-$  and  $2^1A_g^-$  states. Furthermore, it was found that both the dipole moment of the  $1^1B_u^+$  state and the contribution of  $1^1B_u^+$  in the  $S_1$  state are enhanced as the twist angle of C-C bond is increased. Accordingly, it is considered that 3'-hECN has following excited-state properties: (i) the  $S_1$  state is

dominantly of the  $2^1A_g^-$  character, and it gains an intra-ligand charge transfer (ICT) character due to the contribution of  $1^1B_u^+$ , (ii) the ICT character in the  $S_1$  state is enhanced when the carotenoid is twisted with respect to the central C-C bond of the polyene chain. As for the environmental effects, both the dipole moment of the  $1^1B_u^+$  state and the contribution of  $1^1B_u^+$  in the  $S_1$  state are greater in the point charge model, in which the phenol and indole are taken into account as point charges, compared to those in the gas phase. Therefore, the hydrogen-bonding effect formed in OCP increases  $1^1B_u^+/2^1A_g^-$  mixing in the  $S_1$  state, which can explain the experimental observation that photoexcited 3'-hECN exhibits ICT emission in OCP but not in organic solvent. Environmental effects of the electrostatic potentials generated by the inactive orange form of OCP and the active red form of OCP are also discussed.

In chapter 3, excited-state properties of the  $[Ru(bpy)_2dppz]^{2+}$  under different binding environments were discussed by MD simulation and TD-DFT calculation. The radial distribution function (RDF) of hydrogen atoms of water ( $H_w$ ) from the nitrogen atoms of the dppz ligand ( $N_{phz}$ ) obtained by MD simulation indicated that the shortest  $N_{phz}-H_w$  distance is 3.0 – 3.8 Å for the  $[Ru(bpy)_2dppz]^{2+}$  bound to DNA, in contrast to the case of isolated complex where the first peak is at a distance around 2.0 Å, corresponding to form hydrogen bond. TD-DFT calculation for the isolated complex and the hydrogen-bonded complex,  $[Ru(bpy)_2dppz(H_2O)_2]^{2+}$ , clarified that  $^3MLCT_{dppz}$  state (dark state) is stabilized due to the hydrogen bond. The discrete models of  $[Ru(bpy)_2dppz(H_2O)_2]^{2+}$  in which water molecules are positioned at 3.0 – 3.6 Å of  $N_{phz}-H_w$  distance have the excited-state properties similar to those of the isolated complex, namely, local interaction between the  $N_{phz}$  and  $H_w$  hardly affect the excited-state properties. These results implied that the complex intercalating/inserting into DNA does not form hydrogen bonds with water, and the  $^3MLCT_{dppz}$  state cannot be stabilized. The lowest  $^3MLCT$  state of the  $[Ru(bpy)_2dppz]^{2+}$  in consideration of the neighboring DNA parts at quantum chemical level was characterized as  $^3MLCT_{bpy}$ . Therefore, it is considered that the  $^3MLCT_{bpy}$  state is related to the strong emission observed for the complex in the presence of DNA. The electrostatic potential generated by the surrounding DNA atoms is rather negative in the dppz part, whereas it is relatively positive in the bpy part. Accordingly, the  $MLCT_{bpy}$  state could be stabilized in the complex bound to DNA.

In chapter 4, a summary of this thesis and future perspective are described. The present study provides an insight into molecular mechanism of light-induced functions for the photofunctional molecules in biomolecules, such as a protein and DNA, by applying quantum chemical calculations to the suitable models. Theoretical chemistry is expected to contribute to development of photochemistry more and more in future, by constructing model systems reasonable for describing photofunctional phenomena and applying appropriate calculation method.