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2025 年度 博士論文要旨

論文題目

電荷移動性の精密制御を通じた蛍光性化合物群の光化学物性制御に関する研究

英文題目

Study on Controlling Photophysical Properties of Fluorescent Organic Compounds through Precise Charge-Transfer Tuning

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Luminescence properties of a material are dominated by its excited-state electronic and chemical structures. The geometry in the electronic excited state generated by the photoexcitation is different from that in the ground state and, therefore, precise tuning of the excited-state geometry is crucial. Since the excited-state structure is strongly influenced by intramolecular charge-transfer character, charge-transfer tuning provides an effective strategy for controlling spectroscopic and photophysical behaviors. The primary aim of this dissertation is to develop molecular systems in which structures in both the ground and excited states are systematically and continuously varied, in order to clarify the factors determining the photophysical properties of fluorescent organic compounds. Specifically, the present study focuses on bonding patterns, dihedral angles, and solvation structures that are highly sensitive to intramolecular charge-transfer transitions, with the goal of identifying the structural and electronic determinants of emission behavior in the excited state.

Excited-state intramolecular proton transfer (ESIPT) is an excited-state isomerization process in which a hydrogen atom or ion migrates to a different position in a molecule. It is expected that the ESIPT process corresponds to an intramolecular acid–base reaction between the photoacidic and photobasic moieties and that the proton-transfer process can be controlled by tuning the charge-transfer character in the ESIPT-type molecular skeleton. 10-Hydroxybenzo[*h*]quinoline (HBq), an ESIPT-type molecule exhibiting obvious fluorescence even in a dilute solution, was employed as the core skeleton to perform systematic modulation and evaluation, and a series of derivatives having phenyl groups with a various electron-donating and -withdrawing substituent R at the 4-position (4-Rphenyl group: R = -NMe₂, -OMe, -Me, -H, -F, -Cl, -CF₃, -CN, -NO₂) was designed and synthesized (Figure 1).

In Chapter 2, structural and photophysical characteristics of derivatives in which the 4-Rphenyl groups were introduced at 7- and 9-positions, the proton-donating part of HBq (**7,9-HBqNO₂**), were evaluated. Single-crystal X-ray analyses and DFT calculations suggested that all the derivatives adopt the *enol* form with an intramolecular hydrogen bond in the ground state. The derivatives exhibited an obvious visible absorption band at around 400 nm and orange–red fluorescence in dichloromethane at room temperature (Figure 3(b)). The observed fluorescence from the derivatives with R = -NMe₂ to -CN was predominantly due to the ESIPT process triggered by charge-transfer transitions in the HBq moiety, and the charge-transfer character was precisely controlled by the electron-donating or -withdrawing nature of the substituent R. In contrast, **7,9-HBqNO₂** with strongly electron-withdrawing nitro groups showed distinct spectroscopic and photophysical features, where the S₁ transition involved charge transfer from the HBq moiety to the 4-nitrophenyl group. Consequently, **7,9-HBqNO₂** emits from a non-ESIPT excited state stabilized by solvation and twisting of the 4-nitrophenyl group (Figure 2). These results indicate that the electronic

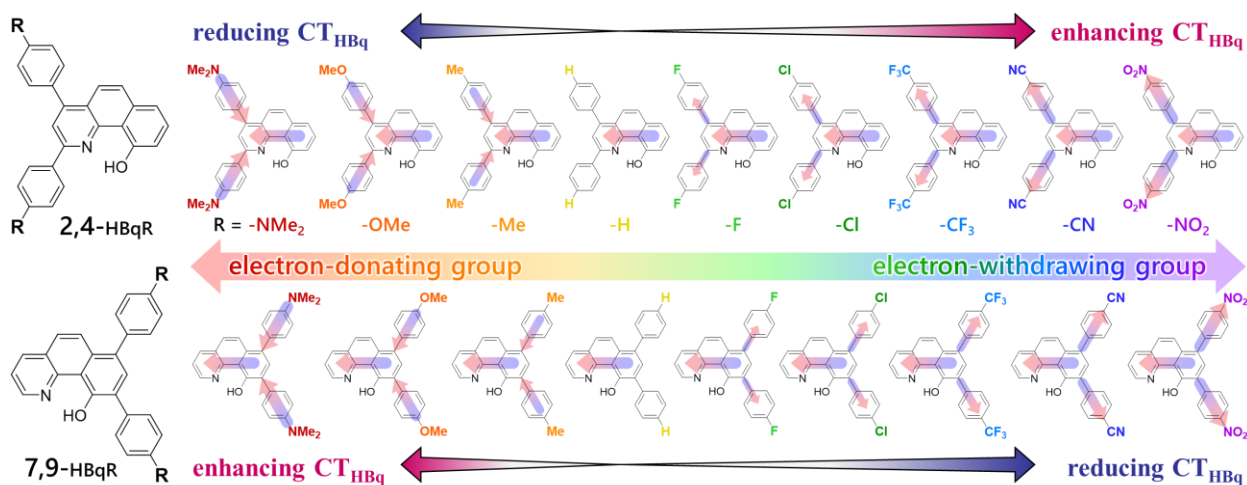


Figure 1. Chemical structures and conceptual scheme of 2,4-HBqR and 7,9-HBqR.

properties of the substituents lead to distinct structural changes in the excited state, even within the same molecular skeleton, and that the redistribution of charge at both the proton-donating and proton-accepting moieties upon photoexcitation is essential for the ESIPT process. The excited-state geometry of the derivatives could be further modulated by an addition of a Brønsted acid, resulting in intensely fluorescent non-ESIPT protonated forms. The introduction of 4-Rphenyl groups altered the ground-state basicity of the HBq skeleton. Notably, **7,9-HBqNMe₂** with proton-accepting dimethylamino groups, exhibited multicolor fluorescence spanning the near-infrared to blue region as a function of the concentration of acid through stepwise protonation of the substituents and the HBq moiety. These results demonstrate that systematic tuning of the electronic structures in both ground and excited states enables precise control over the ESIPT process and fluorescence properties. The findings highlight that the photoacidity and photobasicity of the HBq moiety are critical factors in determining the excited-state geometry and emission behavior.

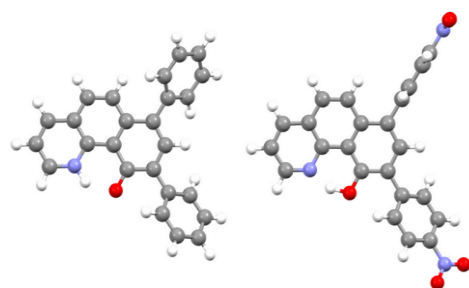


Figure 2. S₁-Optimized geometries of 7,9-HBqH (left) and 7,9-HBqNO₂ (right).

Chapter 3 focused on controlling photophysical properties through precise tuning of the charge-transfer in the HBq moiety (CT_{HBq}). The electronic structures and photophysical properties of the HBq derivatives with the 4-Rphenyl groups at the proton-accepting moiety (**2,4-HBqR**) were evaluated and compared with those of **7,9-HBqR** (Figure 3). Through the electronic nature and position of the substituents, the CT_{HBq} character of a derivative was successfully modulated, allowing precise control over the driving force for the proton transfer and the resulting fluorescence characteristics. The ¹H- and ¹³C-NMR spectra and ground-state optimized geometries suggested that hydroxy protons of reducing-CT_{HBq} compounds in ground states were located closer to imine nitrogen than those of enhancing-CT_{HBq} compounds. These derivatives exhibited orange–red ESIPT-type fluorescence even in dilute solution. Upon reducing CT_{HBq}, fluorescence from a derivative became high-energy, and the absorption–fluorescence energy difference was decreased. It suggests small driving force of the proton-transfer process in the reducing CT_{HBq} derivatives, consistent with non-ESIPT excited state of **7,9-HBqNO₂** in Chapter 2. The S₁-state geometry optimization for **2,4-HBqNMe₂** by the TD-DFT method was converged at both *enol* and *keto* forms, dependent on the initial structure of the calculation whereas those for the other derivatives gave the *keto* forms. The excited-state geometry of **2,4-HBqNMe₂** was judged as the *keto* form by the solvent-dependences of the fluorescence properties, which were comparable to those of the ESIPT-type **7,9-HBqCN**. The fluorescence quantum yields and lifetimes of the derivatives increased with increasing the fluorescence energy, as controlled by the

decreased nonfluorescence rate constant (k_d) by the energy gap law. Notably, the reducing-CT_{HBq} derivatives showed large fluorescence rate constants (k_f), despite incorporation of substituents expected to suppress CT_{HBq}. The enhanced k_f values arise from increased transition dipole moments of the fluorescence process, attributable to excited-state switching to an enhancing-CT_{HBq} character following proton transfer. Consistent with this mechanistic insight, a derivative designed according to a double reducing-CT_{HBq} strategy exhibited fluorescence more than 15-times brighter than that of HBq in THF, owing to its high quantum yield ($\Phi_f = 0.067$) and strong absorption across the visible region. These results provide a comprehensive understanding of the electronic structures in both the ground and excited states and establish an important molecular design strategy for the development of new ESIPT-type compounds.

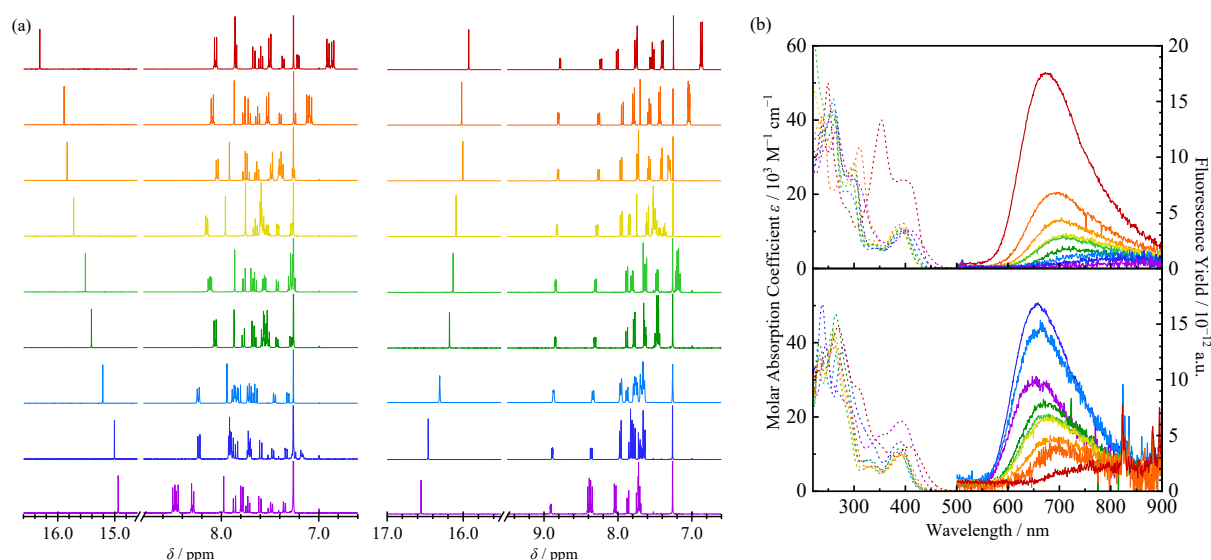


Figure 3. $^1\text{H-NMR}$ spectra of **2,4-HBqR** (left) and **7,9-HBqR** in CDCl_3 (a) and absorption (broken curves) / fluorescence spectra (solid curves, $\lambda_{\text{ex}} = 375\text{--}415\text{ nm}$) of **2,4-HBqR** in THF (top) and **7,9-HBqR** in dichloromethane at room temperature (b). The colors correspond to those indicated in Figure 1.

The intramolecular charge transfer of the 4-nitrophenyl group in **7,9-HBqNO₂**, presented in Chapter 2, provided a concept of the design of the fluorescent molecules with large electric dipole moments. Thus, Chapter 4 targeted the control of fluorescence properties through changes in the solvation structure surrounding the solute in the excited state. A novel fluorescent naphthalene derivative with a 4-nitrophenyl and an electron-donating methoxy group (**1**) was designed and synthesized, together with its 4-nitrophenyl-containing analogues **2** and **3**. In dilute solution, **1** exhibited low-energy absorption and fluorescence with broad spectral shapes, attributable to the charge-transfer transition from the methoxy group to the 4-nitrophenyl group. Derivatives **1–3** showed fluorescent solvatochromism, with the emission color of **1** varying from greenish blue to red depending on the solvent (Figure 5(a)). Solvent-dependent analysis revealed that **1** possesses the largest excited-state electric dipole moment among the derivatives. The large transition dipole moment is explainable by a combination of the strong electron-withdrawing nitro group and the methoxy group with the bridging arylene moiety, facilitating efficient charge transfer. The derivatives exhibited unusual solvent dependences of fluorescence: **1** exhibited weak and short-lived fluorescence in both low- and high-polarity solvents, whereas **2** and **3** were weakly fluorescent in low-polarity solvents. Such unusual solvent dependences originate from a two-step, V-shaped fluorescence-energy dependence of k_d (Figure 5(b)). Although a decrease in k_d with increasing the fluorescence

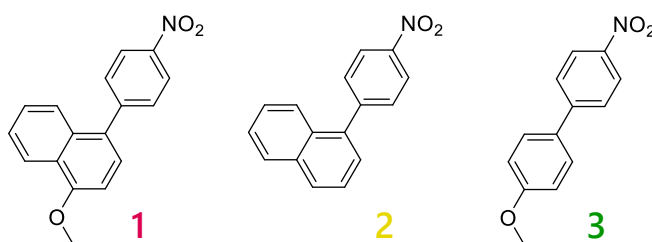


Figure 4. Chemical structures of **1**, **2** and **3**.

energy in the low-energy region can be explained by the energy gap law, a contribution of another nonfluorescence pathway is required to explain the reverse energy gap dependence obtained in the high-energy region. Transient absorption measurements and TD-DFT calculations revealed that the existence of the intersystem crossing to a triplet excited state localized in the 4-nitrophenyl moiety. The results elucidated the reason for nonemissivity of most nitro-containing derivatives and demonstrated that appropriate molecular design, including tuning of the fluorescence energy and choice of the nitroaryl group, enables the development of fluorescent molecules containing nitro groups, effectively extending the charge-transfer character and stabilizing the excited state.

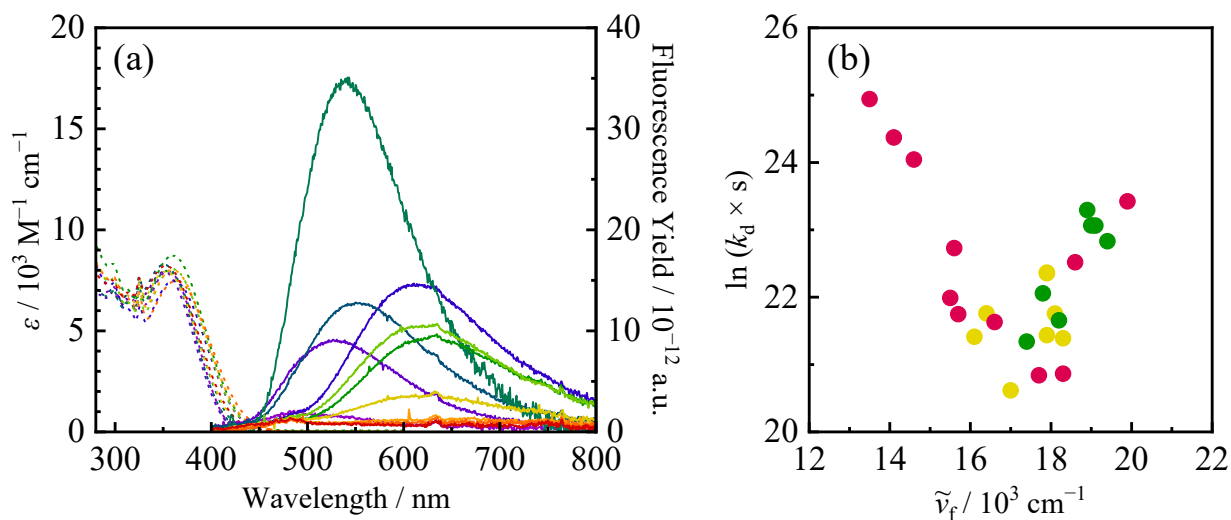


Figure 5. Absorption (broken curves) / fluorescence spectra (solid curves, $\lambda_{\text{ex}} = 375$ nm) of **1** in various solvents (a) and energy gap plot for **1**, **2** and **3** (b). The colors correspond to those indicated in Figure 4.