Theoretical Design of a Molecular Switch with Controlled Hydrogen Bonds: Electronic and Vibrational Spectra of [Co(2,2′-biimidazole)($C_6H_4O_2$)(NH_3)$_2$]$_2$

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The electronic and vibrational spectra of a proton–electron-coupled inorganic complex [Co(Hbim)($C_6H_4O_2$)(NH_3)$_2$]$_2$ having multistable states, were theoretically investigated using density functional theory calculations using B3LYP parameters. The electronic excitation spectrum in the low-spin ground ^1A_g state of the complex has no strong absorption in the visible region (600–700 nm), while in the high-spin $^5A_1$ and ^9A_g complexes, some prominent peaks were predicted in the visible region. Frequency analyses of the ^1A_g, $^5A_1$, and ^9A_g states showed the strong band of the NH stretching vibration at 2690, 2120, and 2770 cm^{-1}, respectively. Based on this, it is possible to distinguish $^5A_1$ from ^1A_g and ^9A_g by measuring IR light absorption at 2120 cm^{-1}, showing that [Co(Hbim)($C_6H_4O_2$)(NH_3)$_2$]$_2$ would be a good candidate for use as optically durable molecular level memory.

The development of molecular memory devices is one of the most exciting and hotly studied fields in photochemistry and nanotechnology. In recent years, many scientists have attempted to construct molecular memory devices with photochromic molecules, e.g. diarylethene,[1–4] azobenzene,[5–8] spiropyran,[9] and fulgide[10,11] derivatives, since these molecules show a digital response to photons and are considered to be suitable for generating the bistable electronic states required to produce the on–off switching states in a molecular memory device. In particular, diarylethene derivatives have been found to be highly successful in controlling digital switching by triggering the on–off switching states with ultraviolet (UV) and visible (vis) irradiation, respectively, making these derivatives potential candidates for use in erasable media.[1]

Unfortunately, however, the photon-mode memories of these organic molecules are prone to loss of optical memory. That is, once the molecular memories have been read using UV (or vis) light, the memories may be erased due to probe-light-induced photochromic reactions. This problem is referred to as "memory degradation in photon mode memory," and is a major hindrance to the construction of reliable molecular memory. Thus, there has been a strong demand for developing new memory-molecules and appropriate techniques to read the photon-mode memory of these molecular systems without memory degradation.

Recently, from a quantum chemical point of view, we have introduced a new class of molecular memory: proton–electron-coupled molecular memory, which can be read without the use of a UV–vis probe.[12,13] In these studies, we have proposed an inorganic complex dimer [Co(Hbim)($C_6H_4O_2$)(NH_3)$_2$]$_2$ as a candidate for such proton–electron-coupled molecular memory, a complex having three stable energy minima in the ^1A_g, $^5A_1$, and ^9A_g states. An indirect memory reading technique using IR probe light, which can be established only with the proton–electron-coupled inorganic complex, was also proposed in these studies.[12,13] In this paper, we will investigate the electronic and vibrational spectra in the multistable states of the complex [Co(Hbim)($C_6H_4O_2$)(NH_3)$_2$]$_2$, as predicted by density functional theory calculations, and this will be used to find methods for reading and writing molecular memory on the proton–electron-coupled inorganic complex dimer.

Theoretical Design of Proton–Electron-Coupled Molecular Memory

As mentioned in the previous section, the indirect detection of the electronic state without UV–vis electronic excitation is considered the best method for reading photon mode molecular memory in a stable manner. The question arises therefore, how would it be possible to avoid direct molecular memory detection when using UV–vis excitation?

The essence of optically durable molecular memory reading is to read the memory without causing changes to the electronic states of the molecules. Therefore, if a low-energy IR photon source can be used as a memory probe, it will be possible to construct an optically durable molecular memory system. Based on this requirement, we proposed the idea of a proton–electron-coupled system with controlled hydrogen bonds.[12,13] As is widely known, the strength of a hydrogen bond can be observed by studying IR spectra. Since the strength of a hydrogen bond depends on the surrounding electronic environment, it becomes possible to control the IR spectral pattern if the motions of the proton and electron can be coupled in a single molecule. It is known that proton–electron coupling can be achieved in mixed-valence inorganic complexes linked through complimentary hydrogen bonds, while the introduction of a transition metal (Ni) into the hydrogen-bonded inorganic complex polymer [Ni^{II}(2,2′-biimidazolate)$^-{}_2$] is known to cause the formation of very strong hydro-

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gen bonds.[14–16] Thus, in our search for a hydrogen-bonded complex dimer that has multi-stable electronic states, we opted for the hydrogen-bonded complex dimer $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$.[12,13]

An important point in our design of optically durable molecular memory is the incorporation of a redox-active *o*-benzoquinone (BQ) ligand into the complex. Since the frontier π orbital of BQ is very close to the Co 3d$_\gamma$ orbital in energy, BQ binds to the Co ion to form bistable electronic states with intramolecular charge transfer; Co^{III}–Cat^{2-} ↔ Co^{I}–BQ, Cat^{2-} is the two-electron-reduced form of BQ.[17–20] Combining the intramolecular redox function of BQ with the hydrogen-bonding function of Hbim, we have succeeded in theoretically showing the existence of a controlled hydrogen bond in the hydrogen-bonded inorganic complex dimer $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$.[12,13] In other words, the coupling of the proton and electron motions is established in the complex dimer, and multi-stable electronic states of the complex dimer can be distinguished using an IR probe rather than a UV–vis probe. Thus, the complex dimer $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ can be used as optically durable molecular memory.

Computational Details

As mentioned above, it is already known that the proton–electron-coupled inorganic complex dimer $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ has three energy minima in the ^1A_g, $^5A_1$, and ^9A_g states, respectively. To search the possibility for performing photo-induced memory writing (or re-writing) of the complex, a theoretical study of the electronic excited states of the complex dimer has been recommended. For this purpose, we performed single-point calculations of time-dependent density functional theory (TDDFT)[21] at optimized geometries using a level of TD/B3LYP to predict the electronic excitation spectra of the complex in the ^1A_g, $^5A_1$, and ^9A_g states. Infrared spectra for three ^1A_g, $^5A_1$, and ^9A_g states were also performed at the B3LYP level. All the calculations were performed using the Gaussian 03 software package.[22] The basis sets used in all calculations in this work were SBKJC VDZ ECP for the Co atoms[23] and 6-31G(d,p) for the other (H, C, N, O) atoms.[24]

Results and Discussion

Electronic Spectra. The electronic excitation spectra of $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ in three stable electronic states, ^1A_g, $^5A_1$, and ^9A_g, calculated at the TD/B3LYP level, are shown in Fig. 1. In the spectra, two groups of absorption bands are predicted. The first group is in the ultraviolet region (<300 nm) while the second is in the visible region (600–700 nm). In the ultraviolet region, strong absorption bands, which are assigned to the π–π^* transitions of Hbim and BQ (or Cat), are predicted in the ^1A_g, $^5A_1$, and ^9A_g states. In the visible region, strong absorption peaks, which are assigned to metal-to-ligand charge transfer (MLCT) from the d$_\varepsilon$ orbital of Co to the π orbital of BQ, are predicted in the high-spin $^5A_1$ and ^9A_g states. No absorption band is predicted for the ^1A_g states in the visible region.

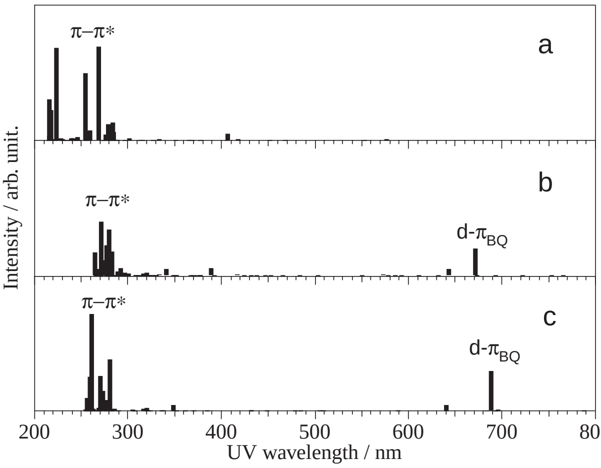

Fig. 1. Electronic excitation spectra of $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ in three stable electronic states, (a) ^1A_g, (b) $^5A_1$, and (c) ^9A_g, calculated at a TD/B3LYP level.

The reason why there is no visible absorption band in the low-spin ^1A_g state is clearly explained by the difference in the electronic structure between the ^1A_g state and the high-spin $^5A_1$ and ^9A_g states. Schematic molecular orbital (MO) diagrams for the ^1A_g, $^5A_1$, and ^9A_g states are shown in Figs. 2–4, respectively. As shown in Figs. 3 and 4, in the high-spin states there exist the single occupied π orbitals (SOMO) of BQ; π_{BQ3} and π_{BQ4} in the $^5A_1$ state and π_{BQ1}, π_{BQ2}, π_{BQ3}, and π_{BQ4}, in the ^9A_g state (nomenclatures of molecular orbitals are given in the figures). Thus, the MLCT electronic transitions from the Co d$_\varepsilon$ orbitals to the BQ π orbitals are expected to arise in the high-spin state. On the other hand, as shown in Fig. 2, there is no SOMO associated with BQ in the low-spin ^1A_g state, while the two BQ ligands in the hydrogen-bonded complex dimer are in the two-electron reduced Cat^{2-} form. Since the Cat^{2-} dianion ligands have no vacant π orbital, there is no MLCT excitation from the Co d$_\varepsilon$ orbital to the Cat π orbital in the low-spin ^1A_g state. Reflecting the difference in the electronic structure between the low- and high-spin states, a kind of photochromism phenomenon accompanied with spin-crossover transition is expected to occur in the inorganic complex $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$.

However, it is to be noted that the difference in the electronic excitation spectra should not be used to obtain electronic structure information, that is, as a memory probe. This is because the UV–vis probe light destroys the molecular memory as mentioned in the introductory section. To read molecular level information written on the complex without memory degradation, the usage of IR absorption is strongly recommended.

IR Spectra. Here, we consider a potential method to detect the difference between these electronic states in an optically durable manner. Our idea of an optically durable memory reading method is based on the use of proton–electron coupling and an indirect electronic state probe employing IR rather than UV–vis light.[12,13]

Theoretically predicted IR spectra of $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ with stable geometries (^1A_g, $^5A_1$, and ^9A_g) are shown in Fig. 5. A strong peak predicted in all states corresponds to an NH stretching vibration associated with the NH···N hydrogen bonds. The frequencies of the NH stretching vibration in the ^1A_g, $^5A_1$, and ^9A_g states were predicted to be 2690, 2120, and 2770 cm^{-1}, respectively. As shown in Fig. 5,

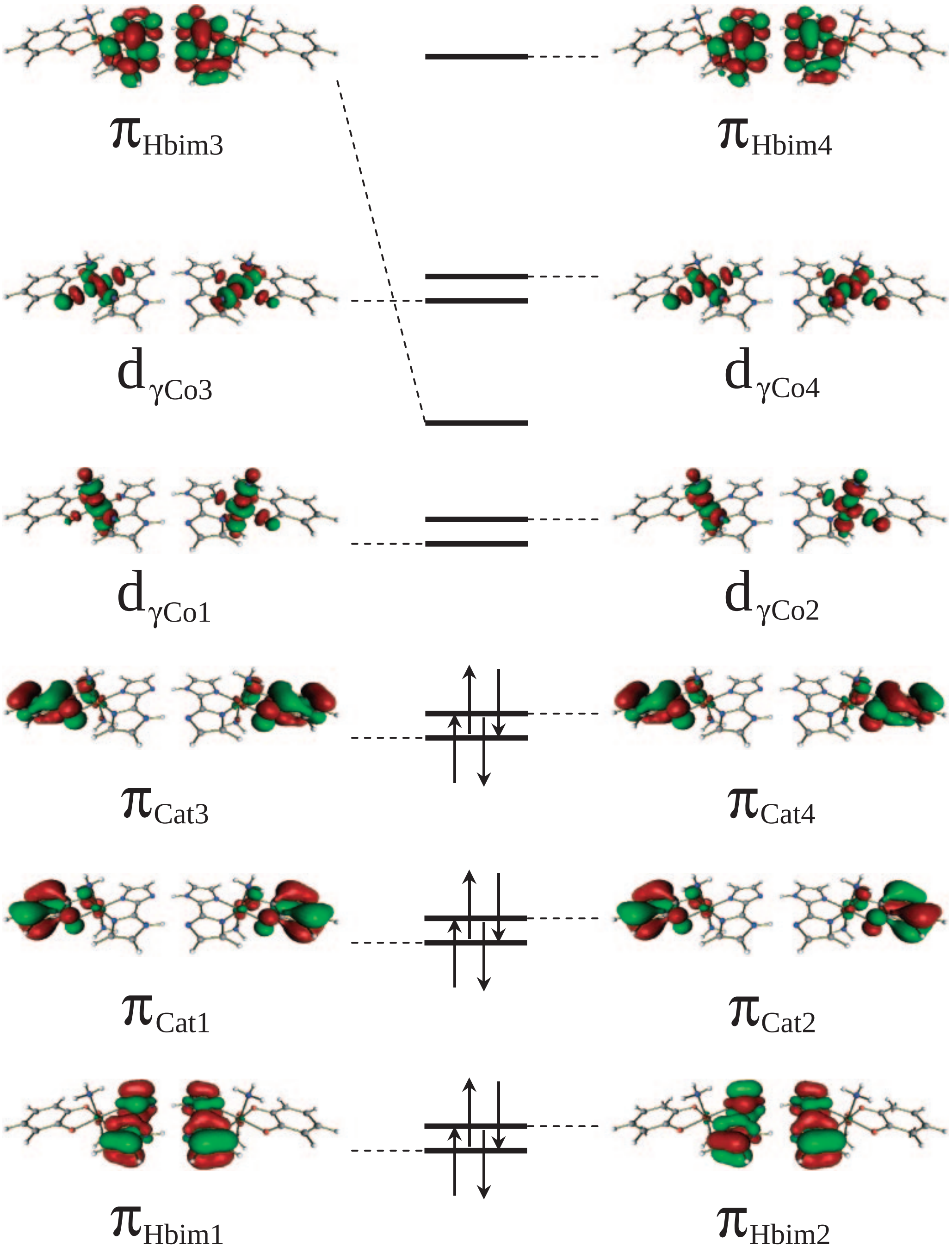

Fig. 2. The d_γ and π orbitals of $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ in the ^1A_g state. Only α-spin orbitals are shown for simplicity, since β-spin orbitals were similar to those of α-spin orbitals.

the NH stretching vibrational frequency of the proton-localized $^5A_1$ state is apparently lower than those of the proton-shared ^1A_g or ^9A_g states. Consequently, IR light of wavelength $2120\,cm^{-1}$ can be used as a probe for the $^5A_1$ state. It is worth mentioning that the IR probe does not excite the complex to its electronic excited states. This means that using the IR probe for the $^5A_1$ state would be a good approach to achieve an optically durable molecular level memory. The reason the frequency of the NH vibration in the $^5A_1$ state is lower than those in the ^1A_g or ^9A_g states is clearly explained by the NH stretching potential energy surface. The anharmonicity of the one-dimensional potential surface is stronger in the $^5A_1$ state than those in the ^1A_g or ^9A_g states. The spectral red shift of the NH hydrogen bond also indicates that the hydrogen bond is stronger in the $^5A_1$ state than those in ^1A_g or ^9A_g states. Reflecting the change in hydrogen-bond strength, the NH and H···N bond lengths in the NH···N hydrogen bond unit are 0.05 Å longer and 0.16 Å shorter, respectively, in the $^5A_1$ state than those in the ^1A_g or ^9A_g states.[13]

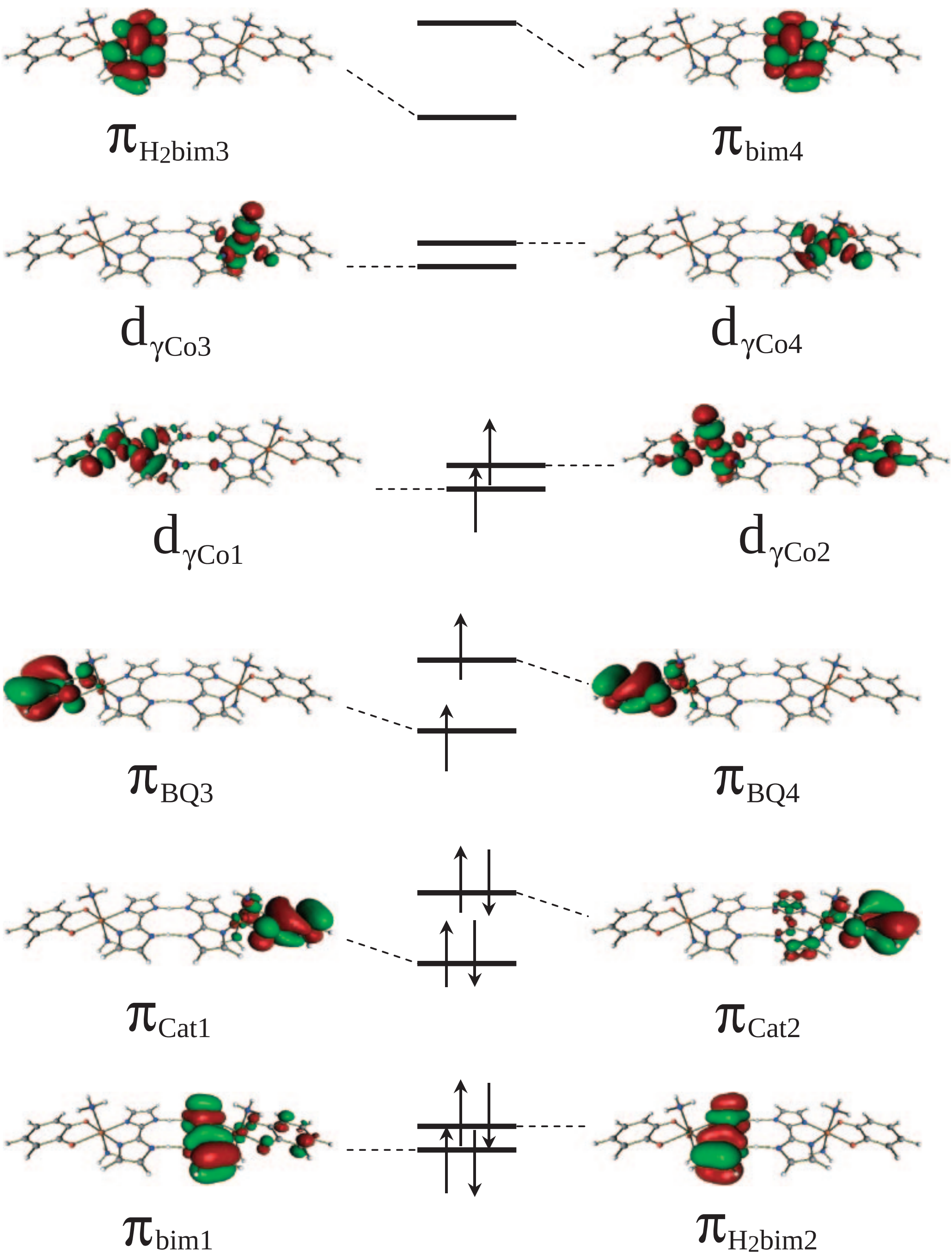

Fig. 3. The d_γ and π orbitals of $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ in the $^5A_1$ state. Only α-spin orbitals are shown for simplicity, since β-spin orbitals were similar to those of α-spin orbitals.

Conclusion

The electronic excited states and vibrational states of a proton–electron-coupled inorganic complex $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ having multi-stable states, ^1A_g, $^5A_1$, and ^9A_g, were theoretically studied using density functional theory calculations with B3LYP parameters.

The electronic excitation spectrum in the ground low-spin ^1A_g state has no strong absorption in the visible region (600–700 nm). On the other hand, in the high-spin $^5A_1$ and ^9A_g states, some prominent peaks were predicted in the visible region. The prominent peaks were assigned to MLCT absorptions from the central Co ion to the redox-active BQ ligand having two vacant (SOMO) π orbitals. Since the redox-active ligand is two-electron reduced to form Cat^{2-} in the ^1A_g state, and there is no vacant π orbital on the Cat ligand, no MLCT state is observed in the ^1A_g state. Thus, the $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ complex shows a kind of chromism phenomena accompanied with spin state conversion.

From the consideration of molecular level photon-mode memory protection, however, the chromism phenomena should not be used to read molecular memory written in the

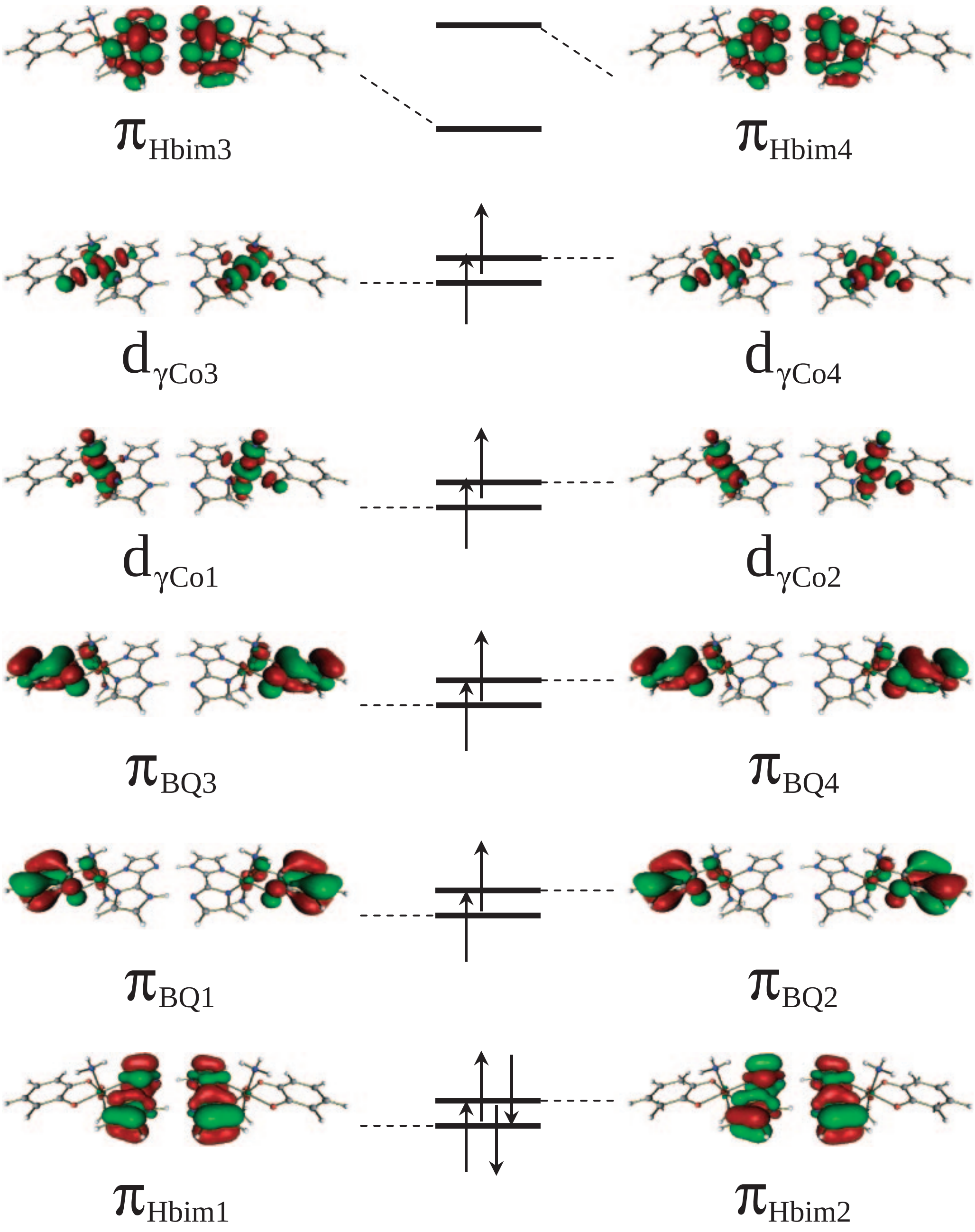

Fig. 4. The d_γ and π orbitals of $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ in the ^9A_g state. Only α-spin orbitals are shown for simplicity, since β-spin orbitals were similar to those of α-spin orbitals.

$[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ complex dimer as would be done in usual photochromic compounds. By using IR rather than UV–vis light to probe the memory, it is possible to read molecular memory on the $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ complex dimer in a stable manner. The frequency analyses of these three states showed that a strong band of the NH stretching vibration is observed at 2690, 2120, and 2770 cm^{-1} in the ^1A_g, $^5A_1$, and ^9A_g states, respectively, and thus we can distinguish $^5A_1$ from ^1A_g and ^9A_g by measuring the IR light absorption at 2120 cm^{-1}, without observing any photo side-reactions. Therefore, $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ is expected to be a good candidate for use in optically durable molecular level memory devices.

In a future study, we will investigate the possibility and methods for writing (and re-writing) molecular memory on this proton–electron-coupled inorganic complex dimer $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ by using spin–orbit interaction calculations.

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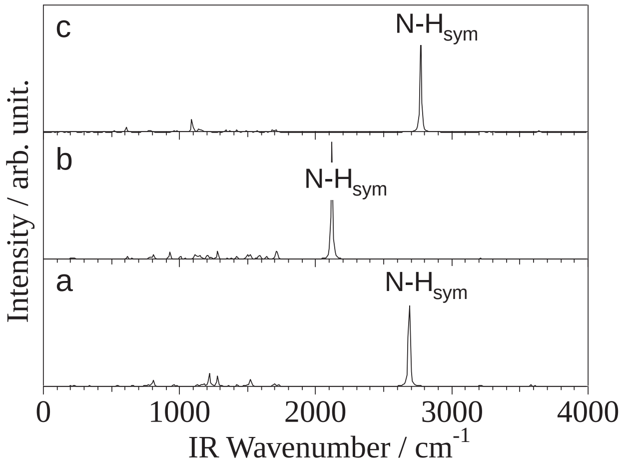

Fig. 5. Theoretically predicted IR spectra at the B3LYP level of (a) the ^1A_g, (b) $^5A_1$, and (c) ^9A_g states. A strong band in each state corresponds to the NH stretching vibration of hydrogen-bonded NH···N units.

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