Theoretical Design of a New Optical Durable Molecular Switch

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A new inorganic molecule that can be used as a new optical durable molecular switch was theoretically designed in the framework of density functional theory. Two energy minima were found in the molecule, and their electronic states were ^1A_g and $^5A_1$, respectively. The predicted infrared spectra in each state showed that the new inorganic molecule have quite different spectra. This means that the molecule can be used as an optical durable molecular switch.

In photochemistry, organic photochromic molecules, e.g. diarylethene, azobenzene, spiropyran, and fulgide, have been widely known and extensively studied. In particular, diarylethene derivatives have succeeded in controlling digital switching by irradiation with ultraviolet and visible light and are expected to function as an erasable media.[1] Unfortunately, however, the photon mode memories of these organic molecules have a fault in protecting their optical memories. That is, once we read the memories by using ultraviolet or visible light, the memories are erased by the probe light. As such, there has been a strong demand for developing new molecules and techniques to read optical memory without memory-degradation.

In this letter, we describe a type of molecule that can function as a better optical switching device. Our discussion is based on a framework of the molecular orbital theory using density functional theory (DFT) calculations at the B3LYP level (geometry optimizations and frequency analyses). Multiconfiguration calculations at the CASSCF(12,12) level were also performed to verify the single configuration pictures of the B3LYP calculations. Eight π orbitals of ligands and four d orbitals of center metal ions were chosen as active orbitals, since these orbitals were around HOMO–LUMO and energetically very close. The CASSCF(12,12) CI vector showed that there is just one important configuration (the weight is over 90% in each state) and the B3LYP results were sufficient to discuss the geometrical and spectral changes of the molecule. The basis sets used in the whole calculations were CEP-31G for the Co atom and 6-31G(d,p) for the others (H, C, and N atoms). All the B3LYP and the CASSCF calculations were performed using Gaussian 03[2] and MOLPRO 2002[3] program packages, respectively.

To construct the molecular optical switch described above, we focused on an inorganic complex, $[Co(C_6O_2H_4)_2(1,10\text{-phenanthroline})]$,[4] that exhibits valence-tautomeric interconversion (low-spin: $[Co^{III}(Sq)^-(Cat)^{2-}(1,10\text{-phenanthroline})] \rightleftarrows$ high-spin: $[Co^{II}(Sq)^-{}_2(1,10\text{-phenanthroline})]$, where $(Sq)^-$ and $(Cat)^{2-}$ mean $(C_6O_2H_4)^-$:*o*-Semiquinonate and $(C_6O_2H_4)^{2-}$: *o*-Catecholate, respectively). There have been many experimental and theoretical studies about the valence-tautomeric interconversion.[4,5] The two valence-tautomeric interconversion states can thus be used as switch on-off states. However, if we use a visible light probe to detect the valence-tautomeric interconversion of $[Co(C_6O_2H_4)_2(1,10\text{-phenanthroline})]$, it will change the electronic states, resulting in memory degradation. Since probing the electronic state of the photoswitching molecule without changing its electronic state is essential to optical durable molecular switches, we must consider other ways to detect valence-tautomeric interconversion.

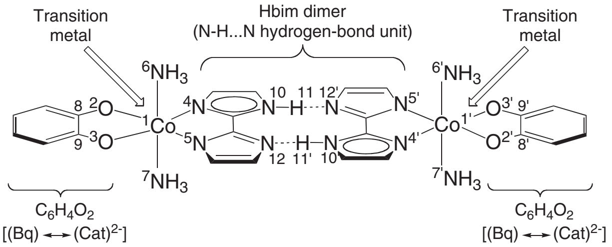

Figure 1. Schematic geometry of photoswitching molecule: $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$.

We hypothesized that the use of infrared light would be a good approach to optically detecting the valence-tautomeric interconversion. Different from ultraviolet or visible light, infrared light can detect the change in electronic states as a change in molecular vibrations without changing the electronic states. The next step was to install a functional ligand whose infrared activity can be controlled by the change of electronic states. The functional ligand that we focused on was 2,2′-biimidazolate (Hbim).[6–8] $Hbim^-$ is a ligand that can form a dimer with N–H···N hydrogen bonds (see Figure 1). In our previous study, it was shown that the Hbim–transition metal complexes have the potential of controlling the strength of the N–H···N hydrogen bonds by a redox reaction of the transition metal.

We therefore designed an inorganic complex, $[Co(Hbim)(C_6O_2H_4)(NH_3)_2]_2$ (see Figure 1). Note that the complex is neutral, making it possible to easily use without choosing any counter ion. The complex dimer is a promising molecule that has bistable states, $[Co^{III}(Hbim)^-(Cat)^{2-}(NH_3)_2]_2$ (^1A_g state: low-spin: C_{2h} symmetry) and $[Co^{I}(Hbim)^-(Bq)(NH_3)_2][Co^{III}(Hbim)^-(Cat)^{2-}(NH_3)_2]$ ($^5A_1$ state: high-spin: C_{2v} symmetry, where Bq is neutral $C_6O_2H_4$: Benzoquinone). The oxidation number of metals and ligands were determined by counting the number of occupied d orbitals of Co and π orbitals of $C_6H_4O_2$. The energy difference between these low-spin and high-spin states found to be 0.7 kcal mol^{-1}. In the high-spin $^5A_1$ state, one monomer unit: $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]$ in the dimer $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ is converted to a high-spin state. Although a symmetric geometry (C_{2h} symmetry), in which both of the two monomer units are excited, was also considered (high-spin state), its energy was estimated to be 22.3 kcal mol^{-1} less stable than the antisymmetric geometry (proton-localized C_{2v} symmetry). To stabilize both the low-spin and high-spin states, it is important to enlarge the magnitude of the geometrical change in the spin-crossover reaction.[9] Geometrical parameter changes between the singlet and quintet states were estimated to be sufficiently large (see Table 1) to stop tunneling deactivation processes from the $^5A_1$ state to the ^1A_g state. In particular, it has been thought that the change of the metal-to-ligand bond lengths (Δr in Table 1) determine the optical stability of the photoinduced spin-crossover state (light-induced excited spin state trapping: LIESST). The Δr values of almost all the spin-crossover complexes that exhibit the LIESST effect are larger than ca. 0.18 Å. The Δr values of $[Co(Hbim)(C_6O_2H_4)(NH_3)_2]_2$ were larger than 0.18 Å, thus the complex has the possibility of achieving LIESST and protect optical memories.

Table 1. The optimized geometry of $[Co(Hbim)(C_6H_4O_2)(NH_3)_2]_2$ at the B3LYP level

State	^1A_g (low-spin)	$^5A_1$ (high-spin)	
Electronic configuration	Co^{3+}-Co^{3+} $3d^6$-$3d^6$	Co^{+}-Co^{3+} $3d^8$-$3d^6$	
Bond length[a]/Å			Δr[b]
Co(1)–O(2)	1.884	2.106	0.23
Co(1)–O(3)	1.881	2.106	0.23
Co(1)–N(4)	1.979	2.160	0.18
Co(1)–N(5)	1.968	2.160	0.19
Co(1)–N(6)	1.965	2.212	0.24
Co(1)–N(7)	1.965	2.212	0.24
O(2)–C(8)	1.358	1.285	−0.07
O(3)–C(9)	1.359	1.285	−0.07
Co(1′)–O(2′)	1.884	1.886	0.00
Co(1′)–O(3′)	1.881	1.886	0.00
Co(1′)–N(4′)	1.979	1.967	−0.01
Co(1′)–N(5′)	1.968	1.967	0.00
Co(1′)–N(6′)	1.965	1.964	0.00
Co(1′)–N(7′)	1.965	1.964	0.00
O(2′)–C(8′)	1.358	1.357	0.00
O(3′)–C(9′)	1.359	1.357	0.00
N(10)–H(11)	1.057	1.102	0.05
N(12′)···H(11)	1.740	1.581	−0.16
Bond angle[a]/deg.			
N(10)–H(11)–N(12′)	170.2	169.4	
N(10′)–H(11′)–N(12)	170.2	166.4	

[a] The numbering of atoms is shown in Figure 1.
[b] Difference of bond length between ^1A_g and $^5A_1$ states.

Because the N–H···N hydrogen-bond strengths in these complexes are strongly related to the electronic environment around the hydrogen bond,[6,8] the infrared spectra of these two stable forms are quite different from each other (see Figure 2). This difference between the ^1A_g and $^5A_1$ states can be used as a molecular switching probe. In $^5A_1$ state, the distance between Hbim dimer units is 0.16 Å shorter and the N–H bond length is 0.05 Å longer than in ^1A_g state. This is the reason why large red shift occurs in $^5A_1$ state. From the point of view of memory-stability, the infrared probe is better than ultraviolet or visible probes because the infrared light does not change the electronic states. Thus we can read written memories in the complex without memory-degradation.

We have thus shown that the bistable states of $[Co^{III}(Hbim)^-(Cat)^{2-}(NH_3)_2]_2$ and $[Co^I(Hbim)^-(BQ)(NH_3)_2][Co^{III}(Hbim)^-(Cat)^{2-}(NH_3)_2]$ can be used as a new type molecular switch, the memory of which can be read by infrared photons without memory-degradation. The complex theoretically designed in this letter will form a new class of photochromic derivatives and has possibilities for a variety of applications in designing optically durable media for ultrahigh-density optical data storage.

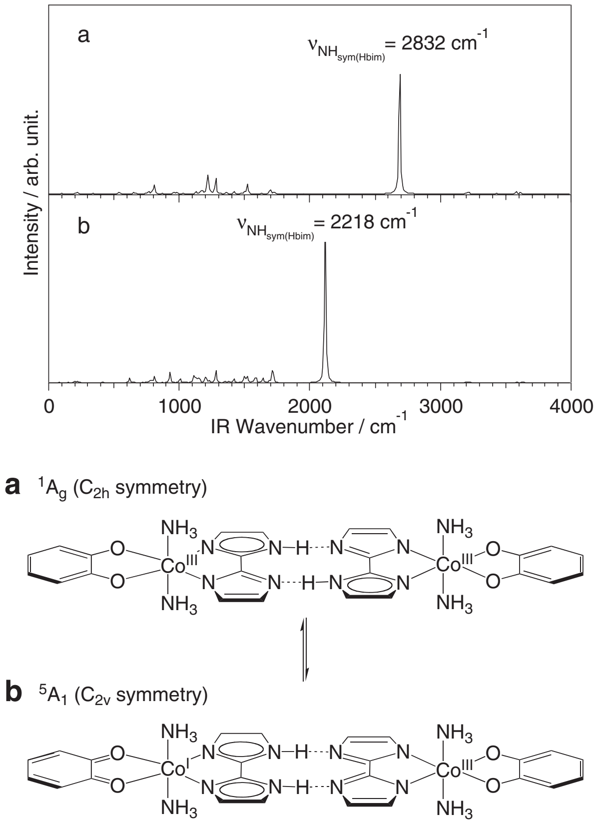

Figure 2. Calculated IR spectra of (a) $[Co^{III}(Hbim)^-(Cat)^{2-}(NH_3)_2]_2$ (^1A_g low-spin state) and (b) $[Co^I(Hbim)^-(BQ)(NH_3)_2][Co^{III}(Hbim)^-(Cat)^{2-}(NH_3)_2]$ ($^5A_1$ high-spin state) at the B3LYP level.

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