Direct EPR Observations of Both Oxidized and Reduced Porphyrin Dimers in the Lowest Excited States: A Novel Analysis of a Homobiradical with a Strong Antiferromagnetic Interaction

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In relation to molecular magnetism,[1] it has been important to clarify magnetic interactions between paramagnetic molecules, and an electron paramagnetic resonance (EPR) method has been shown to be useful for this purpose.[2] However, in general, it is very difficult to examine the magnetic properties of species exhibiting strong antiferromagnetic interactions among spin sites. For example, a pair of molecules in the doublet ground state does not exhibit any steady-state EPR signals, when the antiferromagnetic interaction ($2|J|$) is much larger than the Boltzmann energy (kT). If this kind of electronic state could be observed by means of EPR, we may obtain novel and valuable information on the magnetic properties.

We report here the first EPR study on a homobiradical with a strong antiferromagnetic interaction ($2|J| \gg kT$). The examined molecule is bis(tetra-*tert*-butyltetraazaporphinato)lutetium (III) (Lu-(TAP)$_2$) (Chart 1), which exhibits a useful electrochromism over several steps.[3,4] [Lu(TAP)$_2$]$^+$, an oxidized form of [Lu(TAP)$_2$]^0 radical initially synthesized, corresponds to a dimer of TAP$^-$ radicals.[4,5] It is known for this kind of double-decker dimers that the two porphyrin radicals show a strong antiferromagnetic interaction, resulting in an absence of a steady-state EPR signal.[5] Using a time-resolved EPR (TREPR) method, however, we have succeeded in observing a triplet EPR spectrum consisting of two TAP$^-$ radicals, which exemplifies a novel approach for clarifying antiferromagnetic interactions. Furthermore, TREPR measurements have been carried out for [Lu(TAP)$_2$]^0 and [Lu(TAP)$_2$]$^-$. Electronic structures and excited-state dynamics are compared among [Lu-(TAP)$_2$]$^+$, [Lu(TAP)$_2$]^0, and [Lu(TAP)$_2$]$^-$, and this comparison illustrates the utility of TREPR for examining excited-state properties in various oxidation states.

[Lu(TAP)$_2$]^0 and ZnTAP were synthesized from H$_2$TAP (Aldrich) following the method reported previously.[3] Reduction and oxidation of [Lu(TAP)$_2$]^0 were performed by adding tetrabutylammonium hydroxide and bromine, respectively, and were confirmed by UV–vis absorption spectra.[3] TREPR and steady-state EPR measurements were described previously.[6] Simulation spectra were calculated following the procedure already reported.[7]

Steady-state EPR spectra of [Lu(TAP)$_2$]$^+$, [Lu(TAP)$_2$]^0, and [Lu(TAP)$_2$]$^-$ are shown in Figure 1. For [Lu(TAP)$_2$]^0 consisting of diamagnetic TAP^{2-} and TAP$^-$ radical, an EPR signal is seen at around $g = 2.002$, without hyperfine splitting.[3,5,8] On the other hand, [Lu(TAP)$_2$]$^+$ consists of a pair of TAP$^-$ radicals, but it does not exhibit any steady-state EPR signals except that from the remaining traces of [Lu(TAP)$_2$]^0, even at room temperature.[5] This lack of EPR signal reflects the strong antiferromagnetic interaction between the two TAP$^-$ radicals, which originates from the large overlap between the $a_{1u}{}^A$ and $a_{1u}{}^B$ orbitals. That is, the ground state of [Lu(TAP)$_2$]$^+$ exhibits diamagnetism (the singlet ground state), and two electrons

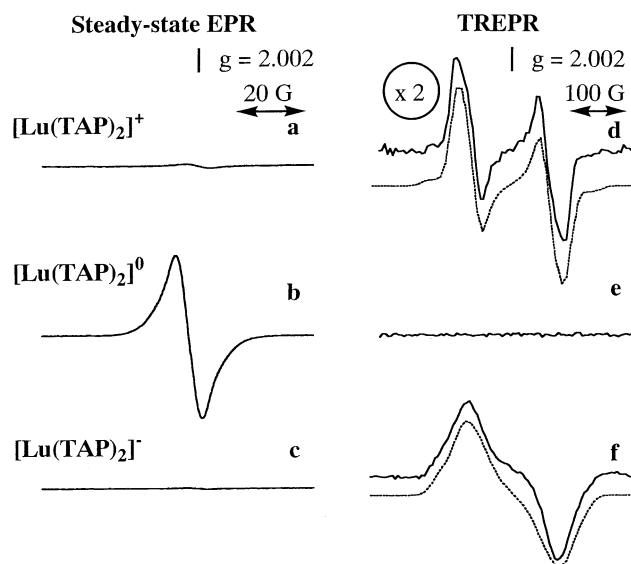**Figure 1.** Steady-state (**a**, **b**, **c**: solid lines) and time-resolved (**d**, **e**, **f**: solid lines) EPR spectra of [Lu(TAP)$_2$]$^+$ (**a**, **d**), [Lu(TAP)$_2$]^0 (**b**, **e**), and [Lu(TAP)$_2$]$^-$ (**c**, **f**) at 20 K. TREPR spectra were measured at 0.9 μs after laser excitation. Simulation spectra (**d**, **f**: broken lines) were calculated using the parameters described in the text.
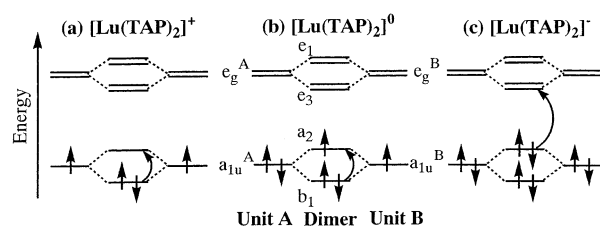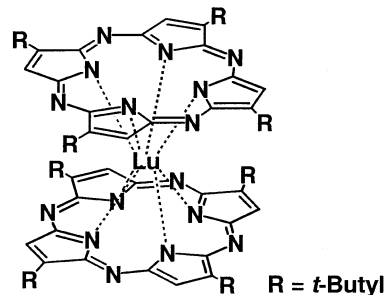

Figure 2. Molecular orbital diagrams of [Lu(TAP)$_2$]$^+$ (a), [Lu(TAP)$_2$]^0 (b), and [Lu(TAP)$_2$]$^-$ (c).

Chart 1

R = *t*-Butyl

are in the bonding b_1 orbital (Figure 2). In the case of [Lu(TAP)$_2$]$^-$, since two diamagnetic TAP^{2-} ligands constitute this reduced form, no EPR signal can be observed.

TREPR spectra of [Lu(TAP)$_2$]$^+$, [Lu(TAP)$_2$]^0, and [Lu(TAP)$_2$]$^-$ are shown in Figure 1. Although no TREPR signal is seen for [Lu-

$(TAP)_2]^{0,9,10}$ we have succeeded in observing the TREPR spectrum of $[Lu(TAP)_2]^+$ in the lowest excited triplet (T_1) state, which is different from those of H_2TAP, ZnTAP, and $[Lu(TAP)_2]^-$.[11] This TREPR spectrum was reproduced using EPR parameters, $D = -0.480$ GHz, E $= 0.050$ GHz, and selective intersystem crossing (ISC) from the lowest excited singlet (S_1) state to the y sublevel of the T_1 state ($P_x:P_y:P_z = 0:0.7:0.3$).[7,12] To clarify the electronic structure of the T_1 state, we have calculated the D value of the (b_1a_2) configuration. Here, the D value of the (b_1a_2) configuration is reasonably transformed into a magnetic dipole−dipole interaction between the a_{1u}^A and a_{1u}^B orbitals under a half-point charge approximation.[13] Assuming the interplanar distance is 3.2 Å,[14] the D value was evaluated as -0.456 GHz, which reproduces excellently the experimental D value (= -0.480 GHz). The T_1 state of $[Lu(TAP)_2]^+$ is clearly assigned to the $^3(a_{1u}^A a_{1u}^B)$ configuration (or $^3(b_1a_2)$). To the best of our knowledge, this is the first EPR observation of a homobiradical with a strong antiferromagnetic interaction $(2|J| \gg kT)$. In addition, the lowest excited state of the oxidized form of double-decker porphyrin dimers was experimentally characterized for the first time.[4,5,10,15−18]

For $[Lu(TAP)_2]^-$, the T_1 TREPR spectrum was reproduced using EPR parameters $D = 0.405$ GHz, $E = 0.065$ GHz, and $P_x:P_y:P_z = 0: 0.4: 0.6$. The D value of $[Lu(TAP)_2]^-$ is much smaller than that (= 0.915 GHz) of the corresponding monomer, ZnTAP. Two kinds of interactions, exciton (EX) and charge resonance (CR) interactions, exist in a T_1 dimer consisting of two identical units.[15,16,18] When the constituting TAP planes are parallel, the D value is not influenced by the EX interaction, and therefore, the small D value results from the CR character.[18] The contribution of the CR configuration was evaluated as 0.38 following the method reported previously.[12,18,19]

It is noteworthy that selectivities in the $S_1 \rightarrow T_1$ ISC are different between $[Lu(TAP)_2]^+$ ($P_x:P_y:P_z = 0:0.7:0.3$) and $[Lu(TAP)_2]^-$ ($P_x:P_y:P_z = 0:0.4:0.6$). In analogy with Zn porphyrins,[6,20] the selective ISC of $[Lu(TAP)_2]^-$ is reasonably explained by spin−orbit coupling (SOC) between the d_{xz} and d_{yz} orbitals or between p_x and p_y orbitals on the central lutetium ion, which are admixed with the e_3 and e_1 orbitals of TAP ligands, constituting the S_1 and T_1 states.[15,16] In the case of the (b_1a_2) configuration of $[Lu(TAP)_2]^+$, the electron density of the b_1 and a_2 orbitals is absent on the pyrrole nitrogens and lutetium.[8] That is, the ISC is not influenced by the SOC of the central lutetium ion, and therefore, the selective ISC to the y sublevel occurs due to the SOC between the π and σ orbitals, which are admixed with the b_1 and a_2 orbitals via vibronic coupling.[6,20] It is thus clearly shown that the influences of the central metal ion are dependent on the oxidation states of the TAP ligand.

In summary, we have described a TREPR study on three oxidation states of $Lu(TAP)_2$, where the lowest excited states of the oxidized and reduced forms are quantitatively characterized. In particular, the T_1 $[Lu(TAP)_2]^+$ corresponds to the first EPR observation of a homobiradical with a strong antiferromagnetic interaction. This kind of TREPR application will provide the novel information on antiferromagnetic interactions between paramagnetic species. In addition, since there have been only a few studies on the combined use of the TREPR and electrochemistry,[21] these T_1 TREPR spectra of two different oxidation states are the first and valuable example, exemplifying the utility of TREPR for investigating compounds in various oxidation states, similarly to steady-state EPR.

Supporting Information Available: The negative sign of D and evaluation method of CR character (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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