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THERMALLY ACCESSIBLE TRIPLET STATE IN A PHTHALOCYANINE ASSEMBLY SYSTEM WHICH IS FORMED FROM CROWN-ETHER-SUBSTITUTED LUTETIUM PHTHALOCYANINE DIMER RADICALS IN THE PRESENCE OF POTASSIUM ION

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Abstract A temperature variational ESR measurement was carried out for a phthalocyanine assembly system which is composed of two lutetium phthalocyanine dimer radical. The assembly system, to which we refer as "(2+2) tetramer", is a biradical and shows a typical ESR signal of triplet state in random orientation in solution. The intensity change of the signal corresponding to the triplet state over the range from 8.5K to 60K was undetectablly small. For the determination of the energy levels of the triplet and singlet state, we calculated the exchange interaction term as well as the zero field splitting constant using semiempirical MO of the dimer.

INTRODUCTION

Bis(phthalocyaninato)lutetium radical [$Lu(Pc)_2$] (Pc=phthalocyanine) [1,2] is a face-to-face stacking dimer having an unpaired electron delocalized over two Pc rings.[3] Its intrinsic semiconductivity in single crystal and thin film has been well investigated and established.[3-6] In an attempt to study interaction between the Pc dimer radicals in an isolated environment, we previously synthesized a Pc heterodimer, [Lu(CRPc)(Pc)] (Figure 1), one of whose Pc rings is substituted by crown-ethers on its periphery.[7] The heterodimer forms an assembly, to which we have referred as "(2+2) tetramer" (Figure 2), in the presence of potassium cation in solution.[7] The tetramer formation occurs by sandwiching of potassium ions between crown-ether parts of the heterodimer. Since each dimer has an unpaired electron on its π-orbital, the way how the two unpaired electrons behave in the assembly system was an immediate question. The (2+2) tetramer was found to show a typical ESR spectrum of triplet state in random orientation in solution at 77K.[7] The near IR absorption band of the dimer radical at $7\times10^3 cm^{-1}$, which is assigned to the

transition to a valence resonance state, remains after the tetramer formation. From these results, the (2+2) tetramer was concluded to be a biradical, where the two unpaired electrons exist separately on each dimer site.[7]

In this paper, we discuss the energy levels of the triplet and singlet states which are specified by the orientation of the two electron spins. For the determination of the ground state, we carried out a temperature dependence study of the ESR signal of the (2+2) tetramer at lower than 77K. The intensity change of the signal against the temperature variation, however, was undetectablly small, contrary to the expectation. As a clue for the cause of the invariance, we calculate the energy difference of the two states using the Heitlar-London model. Also the zero field splitting constant of the triplet state is calculated using the same basis set. The ground state electronic structure of the (2+2) tetramer is discussed based on these results.

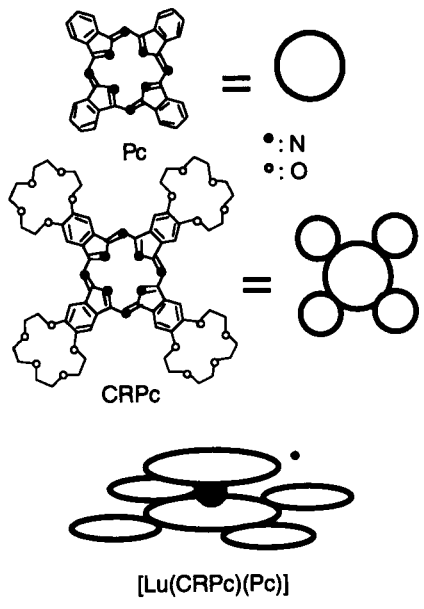

FIGURE 1. Schematic diagram of crown-ether substituted bis(phthalocyaninato)lutetium [Lu(CRPc)(Pc)].

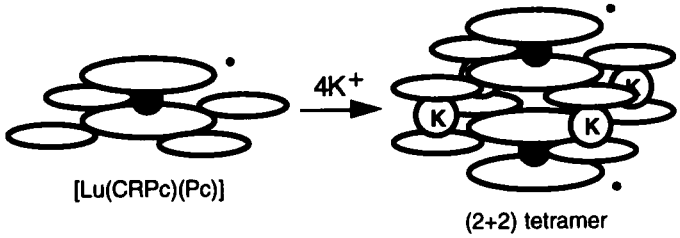

FIGURE 2. The "(2+2) tetramer" formation from the crown-ether substituted lutetium phthalocyanine dimer radical [Lu(CRPc)(Pc)].

EXPERIMENTAL

Temperature variational ESR spectra were measured on a JEOL JES-TE200 operating at X-band frequency equipped with a LTR3X temperature controller. The solvents used for the spectral measurements were purified by distillation.

RESULTS AND DISCUSSION

Figure 3 shows the result of the ESR spectrum measurement at varied temperatures. The tetramer's signal is labeled by "t", and that of residual dimer is "d" in the figure. In contrast to the large temperature dependence of the dimer's signal, which grows by the temperature gets lower, the tetramer's signal did not show significant change both in intensity and line shape. Although the invariantness should be caused by many factors such as relative energy of the singlet and triplet states and relaxation time, it can be said that the energy of the triplet state is either lower than that of the singlet state or, even if higher than the singlet, close to the ground singlet in such a degree that the state can be thermally populated at several kelvin.

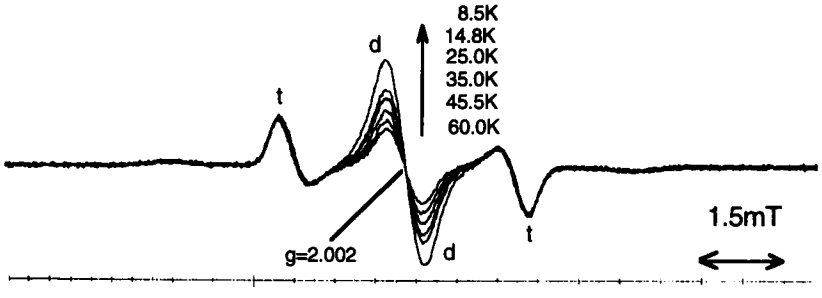

FIGURE 3 Temperature dependence of the ESR spectrum of the (2+2)tetramer. The signal labeled by "t" is of the tetramer, and that by "d" is of the residual dimer. The sample was prepaired by dissolution of [Lu(CRPc)(Pc)] in chloroform and successive addition of an equivolume methanol solution of potassium acetate.

The electronic states of the system composed of two electrons which are in distant orbitals, which we assume the present (2+2) tetramer biradical is, can be well described by the standard Heitler-London treatment. The assumption that the two unpaired electron exist separately is justified by the experimental data that the "valence resonance band" of the dimer radical observed at $7\times10^3\text{cm}^{-1}$ does not disappear by the tetramer formation.[7] Assuming the model where the unpaired electron is subject to a potential which is made by the rest of the electrons and nuclei, the one-electron hamiltonians of the individual dimer *A* and *B* can be written as

$$H_A = -\frac{1}{2}\nabla^2(1) + V_A(1)$$

$$H_B = -\frac{1}{2}\nabla^2(1) + V_B(1)$$

which satisfy the following Schrödinger equations

$$H_A\phi_A = \varepsilon_A\phi_A$$

$$H_B\phi_B = \varepsilon_B\phi_B$$

where ϕ_A and ϕ_B are the orbitals localized on A and B respectively and ε_A and ε_B are the orbital energies. The total hamiltonian of the assembly system AB is

$$H_{AB} = -\frac{1}{2}\nabla^2(1) - \frac{1}{2}\nabla^2(2) + V_A(1) + V_B(1) + V_A(2) + V_B(2) + \frac{1}{r_{12}}$$

The wave functions and their energies of the triplet state are

$$|1,1\rangle = \frac{1}{\sqrt{1-s^2}}|\phi_A\phi_B|,\ |1,0\rangle = \frac{1}{\sqrt{2-2s^2}}\left\{|\phi_A\bar{\phi}_B| + |\bar{\phi}_A\phi_B|\right\},\ |1,-1\rangle = \frac{1}{\sqrt{1-s^2}}|\bar{\phi}_A\bar{\phi}_B|$$

$${}^3E = \langle 1,1|H_{AB}|1,1\rangle = \langle 1,0|H_{AB}|1,0\rangle = \langle 1,-1|H_{AB}|1,-1\rangle$$

Those of singet are

$$|0,0\rangle = \frac{1}{\sqrt{2+2s^2}}\left\{|\phi_A\bar{\phi}_B| - |\bar{\phi}_A\phi_B|\right\}$$

$${}^1E = \langle 0,0|H_{AB}|0,0\rangle$$

Here, s is the overlap integral of ϕ_A and ϕ_B. The exchange interaction defined by

$$J = \frac{1}{2}\left\{{}^1E - {}^3E\right\}$$

is expressed by

$$J = \frac{1}{1-s^4}\Big[(\phi_A\phi_B|\phi_B\phi_A) + s\left\{(\phi_A|V_A|\phi_B) + (\phi_B|V_B|\phi_A)\right\} - s^2\left\{(\phi_A|V_B|\phi_A) + (\phi_B|V_A|\phi_B) + (\phi_A\phi_A|\phi_B\phi_B)\right\}\Big]$$

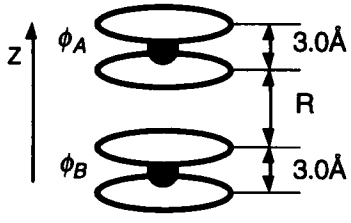

FIGURE 4 The definition of the interplanar distance R and the geometry used for the calculation of the exchange interaction J. ϕ_A and ϕ_B are localized on each dimer, respectively.

Figure 5 shows the calculated values for J at varied distances between the dimers. For the orbitals ϕ_A and ϕ_B, LUMO of a hypothetical molecule $[Lu(Pc)_2]^+$ was employed. The orbitals are obtained by the semiempirical Hartree Fock MO calculation using the same method that we previously used.[9,10] For the potential V_A and V_B which the "core" $[Lu(Pc)_2]^+$ makes, the electric charge from the electron population on a AO was assumed to be a point charge

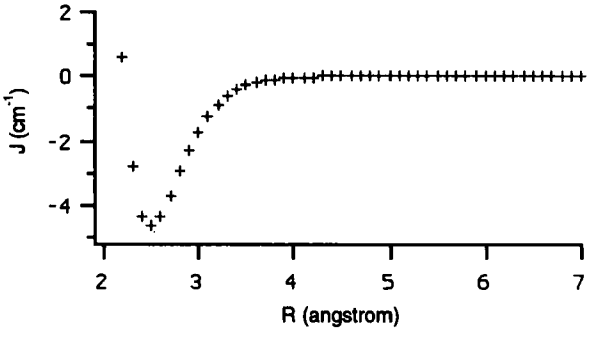

FIGURE 5 The exchange interaction J vs the interplanar distance

placed on the nucleus to which the AO belongs. As seen in the figure, the J takes negative value, and therefore the singlet is the ground state for all distance above 3Å. The distance between the dimers has not been determined experimentally to date. If we apply twice the van der Waals radius of carbon, 3.4Å, which is about the same as the interlayer distance of graphite, J is estimated at -0.43cm^{-1}. For the distance 4.1Å which is suggested by Kobayashi and Lever for the CRPc dimer,[8] which is formed from two [Cu(CRPc)] by the same principle as the present (2+2) tetramer, the exchange term J becomes -0.024cm^{-1}. If this distance is also valid for the (2+2) tetramer, the calculational result indicates that the singlet-triplet energy difference (ca -0.05cm^{-1}) is smaller than the Zeeman splitting of the triplet sublevels (ca 0.3cm^{-1}) by about one order of magnitude under the magnetic field of the present experiment (ca 330mT).

Often zero field splitting is used as a measurement of the average distance between two spins. Using the same MO, the zero field splitting constant D was calculated for the varied distances (Figure 6). Since the tetramer has a D_{4h} symmetry, the term E is set to zero choosing the C_4 axis as the principal axis. The D value is written as [11]

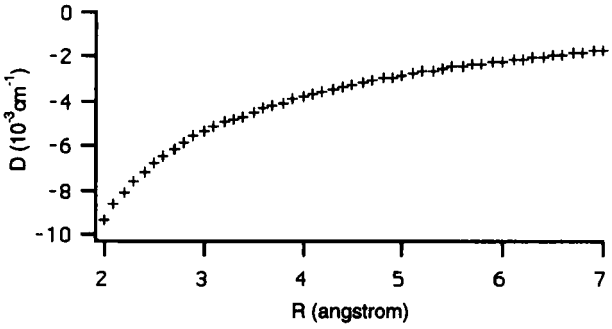

FIGURE 6 The zero field splitting constant D vs the interplanar distance

$$D = -\frac{3}{4}\frac{\mu_0}{4\pi} g^2\beta^2 \left\{ \left\langle \phi_A(1)\phi_B(2) \middle| \hat{D} \middle| \phi_A(1)\phi_B(2) \right\rangle - \left\langle \phi_A(1)\phi_B(2) \middle| \hat{D} \middle| \phi_A(2)\phi_B(1) \right\rangle \right\}$$

where

$$\hat{D} = \frac{3z_{12}^2 - r_{12}^2}{r_{12}^5}$$

The second term of the former equation is negligible because we are dealing with orbitals ϕ_A and ϕ_B which are distant to one another. The first term is expanded using LCAO MO coefficients C_{iA} and C_{jB}, and approximated as follows

$$\sum_{ijkl} C_{iA}C_{jA}C_{kB}C_{lB}\left(\chi_i\chi_j \middle| \hat{D} \middle| \chi_k\chi_l\right) \approx \sum_{ij} C_{iA}^2 C_{jB}^2 \left(\chi_i\chi_i \middle| \hat{D} \middle| \chi_j\chi_j\right) \approx \sum_{ij} C_{iA}^2 C_{jB}^2 \frac{3z_{ij}^2 - r_{ij}^2}{r_{ij}^5}$$

where r_{ij} is the distance between two centers i and j and z_{ij} is the z component of r_{ij}. Here

we used point dipole approximation for each AO integral in the second term. As seen in the figure, D is calculated at $0.0034cm^{-1}$ for the interplanar distance 4.1Å and $0.0046cm^{-1}$ for 3.4Å while the observed value is $0.0040cm^{-1}$. This result is significantly improved from the simple point dipole approximation which gives the value 8.7Å as the mean distance between the dipoles, which means 5.7Å (8.7Å–3.0Å) for the interplanar distance, by substituting the experimental zero field splitting to the equation,

$$|D| = \frac{3}{2}\frac{\mu_0}{4\pi} g^2 \beta^2 r^{-3}.$$

Unlike the exchange interaction, the zero field splitting constant is shown to be subject to relatively small change with the interplanar distance variance.

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