A Supramolecule Composed of Two Phthalocyanine Dimer Radicals Linked by a Pivot Joint: Synthesis of Mono-15-Crown-5-Substituted Bis(phthalocyaninato)lutetium

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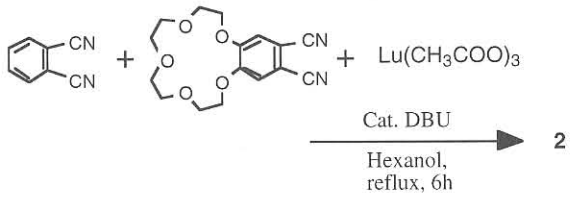
Mono-15-crown-5-substituted bis(phthalocyaninato)lutetium was synthesized. By addition of potassium cation in solution, the phthalocyanine dimer radical formed a supramolecular structure which preserves two unpaired electrons and shows a ESR signal of a triplet state. From observed zero field splitting constant, the structure is likely to be bent rather than straightly linked.

Bis(phthalocyaninato)lutetium[1,2] [$Lu(pc)_2$] (H_2pc = phthalocyanine) is a stable radical which has an unpaired electron delocalized over two pc rings.[3] Its semiconductivity in solid state has been well investigated.[3-6] It is believed that the electric conduction occurs by hopping of the hole from dimer to dimer. Because of its intrinsic electric carrier and magnetic moment, the pc dimer radical is one of expected molecular building blocks for new multi-functional materials. In order to investigate interaction between pc dimer radicals and behavior of two holes in an isolated environment, we previously synthesized a pc heterodimer **1** (Figure 1), one of whose pc rings is substituted by four 15-crown-5 ethers on its periphery.[7] In the presence of potassium cation, the heterodimer forms a biradical supramolecular structure **3** (Figure 2) where four pc rings are placed perpendicular to a common C_4 rotational axis.[7,8] In this letter we report a synthesis of a novel crown-substituted pc heterodimer which forms a supramolecule with a different configuration. Mono-15-crown-5-substituted bis-(phthalocyaninato)lutetium **2** has only one binding hand by which two dimer radicals are linked to form a supramolecule **4**. In contrast to the rigid structure of **2**, **4** has a pivot joint at the potassium cation interposed between two crown moieties. This rotational freedom is expected to give **4** a dynamism in electric and magnetic properties that can be controlled by outer perturbations such as light irradiation.

The synthesis of **2** was achieved as the following scheme.



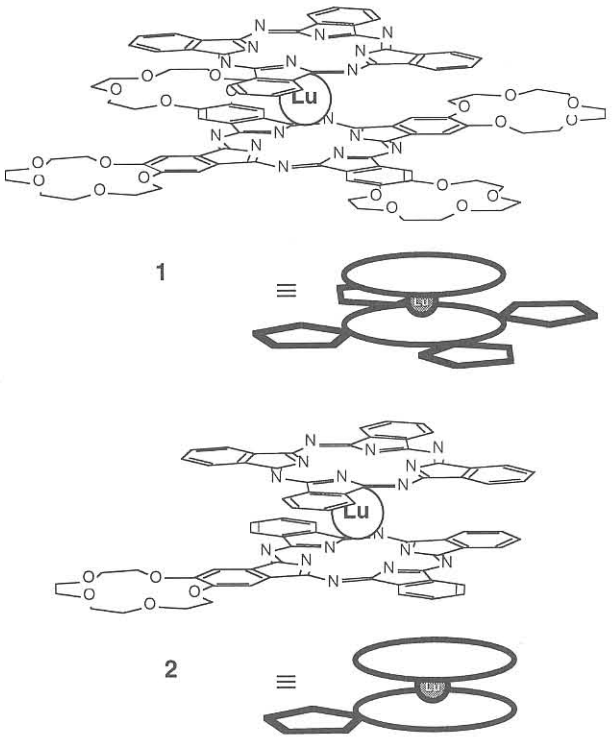


Figure 1. Molecular structure of tetra- and mono-15-crown-5-substituted bis(phthalocyaninato)lutetium.

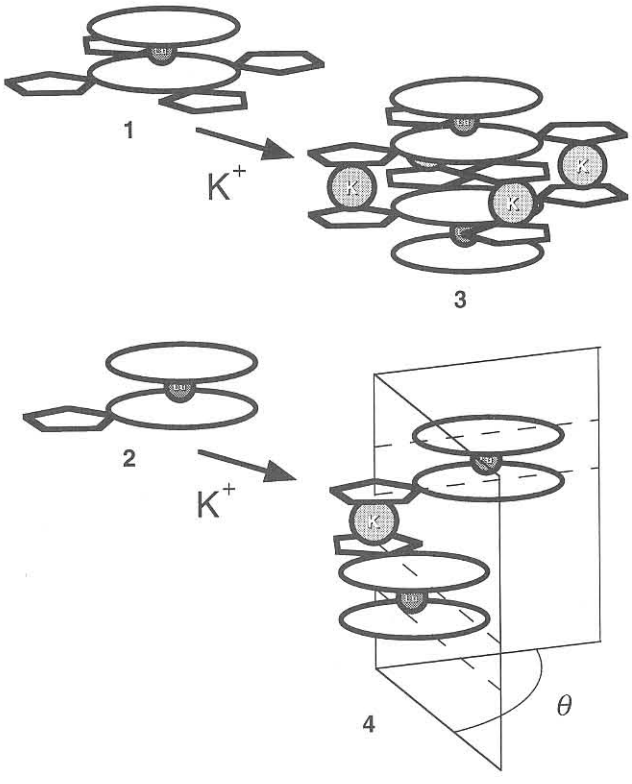


Figure 2. Supramolecular formation induced by potassium cation

Dicyanobenzo-15-crown-5 (1g) and dicyanobenzene (2.81g) were condensed with lutetium acetate (1.33g) in the presence of 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) to give a mixture of non-, mono-, and poly-crown-substituted bis(phthalocyaninato)-lutetium and monomeric phthalocyaninato lutetium complexes. The mixture was concentrated, added to hexane and filtered. The precipitate was extracted by dichloromethane and added to hexane to give a viscous mass. Succeeding reprecipitations by chloroform/hexane yielded 3.3g of powdered crude product, which was then subjected to column chromatography to isolate **2**. First a chloroform solution of the crude product (typically 700mg in 35ml of the solvent) was developed with chloroform on an alumina column (Merck Aluminium oxide 90, particle size 0.063–0.200mm, 5cm diameter, 6cm tall). The first band, which contained radical forms of non-, mono-, and poly-crown-substituted bis(phthalocyaninato)lutetium, was collected, concentrated and added to hexane to give a precipitate (about 120mg from 700mg of the crude product). Following a filtration, the precipitate was dissolved (typically 30mg in 25ml of the solvent) in chloroform/hexane (95/5, v/v) and put on a silica gel column (Merck Silica gel 60, particle size 0.040–0.063mm, 5cm diameter, 6cm tall). Using chloroform/hexane=95/5, non-substituted complex, which did not show any remarkable change in ESR spectrum on addition of CH_3COOK solution of methanol, was first eluted. The second band, which contained only **2**, was eluted with a sufficient separation from the first and third bands. From a single operation of the last procedure, about 8mg of **2** was isolated. Overall yield of **2** was 3%. The compound was identified by elemental analysis and mass spectrum (FAB method on JEOL JMS AX-505HA). Analysis. Calcd(%) for $C_{72}H_{46}N_{16}O_5Lu{\bullet}CHCl_3$: C, 58.08; H, 3.14; N, 14.85. Found(%): C, 58.05; H, 3.33; N, 14.79. MS: m/e 1389.3 (mol. wt. 1389.3 for $C_{72}H_{46}N_{16}O_5Lu$). It was confirmed by the mass spectrum that the sample did not contain non- and poly-15-crown-5-substituted species.

Figure 3 shows ESR spectra of **2** in frozen solution in the absence and presence of potassium cation. Without potassium cation, **2** shows a structureless signal at g=2.0024 in chloroform. The signal is due to the unpaired electron delocalized over π orbitals of the two pc ligands. When methanol was added (Figure 3-(b)), weak signals were observed on both side of the main signal, indicating an occurrence of partial aggregation. By addition of CH_3COOK, a typical ESR spectrum of a triplet state in random orientation was observed (Figure 3-(c)). This clearly shows a formation of supramolecule **4**, which behaves as a biradical. In contrast to the ESR spectral change, absorption spectrum of **2** in solution, which is almost indistinguishable from that of the non-substituted $[Lu(pc)_2]$, did not show any noticeable change by addition of CH_3COOK and/or methanol. This indicates that the two holes are completely preserved in individual pc dimers. Zero field splitting constant $|D|$ of **4** ($\approx$2.9mT, 0.0027cm^{-1}) is smaller than that of **3** ($\approx$4.3mT, 0.0040cm^{-1}).[7,8] In a point dipole approximation, the mean distance between the two electron spins in **4** is estimated at 1.1 times ($=4.3^{1/3}/2.9^{1/3}$) longer than that of **3**, indicating nonzero but moderate value for the pivot angle θ (Figure 3). Using a better model[8] taking into account the orbital shape of the unpaired electrons,[9,10] the

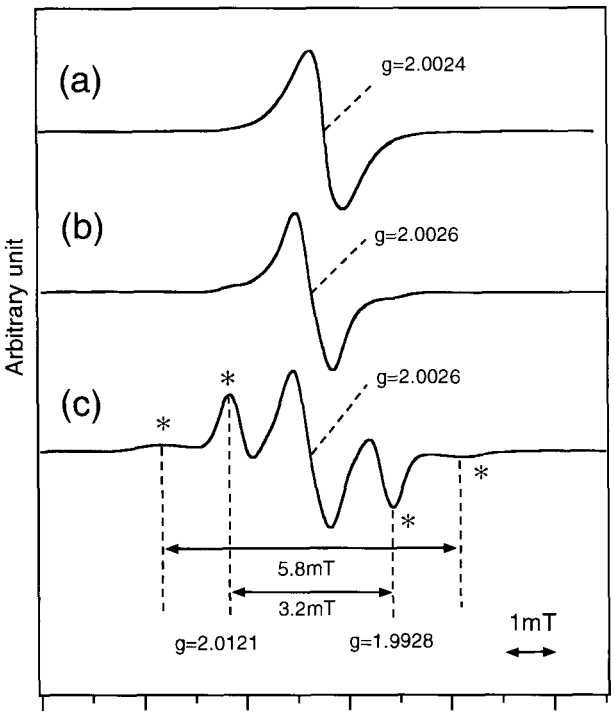


Figure 3. X band ESR spectra of **2** at 77K (a) in chloroform, (b) in chloroform/methanol (2/1, v/v) and (c) with 0.08 mol dm^{-3} of CH_3COOK in chloroform/methanol (2/1, v/v). Concentration of **2** in (b) and (c) is 1.4 $\times$ 10^{-4}mol dm^{-3}. The signal of the supramolecule **4** is labeled by "*".

observed $|D|$ was reproduced when θ is around 25°.[11] From these results, the link is most likely to be bent rather than straight. This contrasts with crystal structure of 2:1 complex of benzo-15-crown-5 and potassium cation:[12] the complex has a center of symmetry, which is on the sandwiched potassium, and its two benzene rings are symmetrically placed with respect to the center. The bent structure of **4** is perhaps due to a stabilization by overlap of pc rings. Details of the calculational results and theoretical consideration for explanation of the bent structure will be reported elsewhere.

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