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ABAB Homoleptic Bis(phthalocyaninato)lutetium(III) Complex: Toward the Real Octupolar Cube and Giant Quadratic Hyperpolarizability

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Ⓢ *Supporting Information*

ABSTRACT: The concept of octupolar molecules has considerably enlarged the engineering of second-order nonlinear optical materials by giving access to 2D and 3D architectures. However, if the archetype of octupolar symmetry is a cube with alternating donor and acceptor groups at the corners, no translation of this ideal structure into a real molecule has been realized to date. This may be achieved by designing a bis(phthalocyaninato)lutetium(III) double-decker complex with a crosswise ABAB phthalocyanine bearing alternating electron-donor and electron-acceptor groups. In this communication, we present the first step toward this goal with the synthesis, crystal structure determination, and measurement of the molecular first-order hyperpolarizability β by harmonic light diffusion, of an original lutetium(III) sandwich complex displaying the required ABAB-type alternation for one face of the cube. This structure is characterized by an intense absorption in the near-IR due to an intervalence transition and exhibits the highest quadratic hyperpolarizability ever reported for an octupolar molecule, $\sqrt{\langle \beta_{HLS}^2 \rangle}_{1907} = 5750 \times 10^{-30}$ esu.

Octupolar molecules, in which symmetry constraints impose a cancellation of the dipole moment, have considerably extended the possibilities of molecular engineering of second-order nonlinear optical molecules by enlarging the dimensionality of the charge transfer. At a structural level, it has been shown that the generic template for octupolar molecules is a cube with an overall tetrahedral symmetry (T_d) (Figure 1)[1] with eight alternating charges at the corners with electronic interactions along the edges of the cube. Starting from this ideal structure, various octupolar geometries (which have been translated into 2D and 3D molecules[2]) can be deduced by projecting the charge or merging one type of charge at the barycenter of the cube. However, a real "cubic" molecule (even if twisted) with eight alternating charges at the corners and delocalization of the charges between the higher and lower planes has not yet been realized. Taking advantage of the unconventional through-space intramolecular charge transfer provided by the paracyclophane framework, Bazan and co-workers described the closest example to date, which contains a paracyclophane core having four *N*,*N*-dialkylamino electron-donor groups at alternate positions of the two benzene rings.[3]

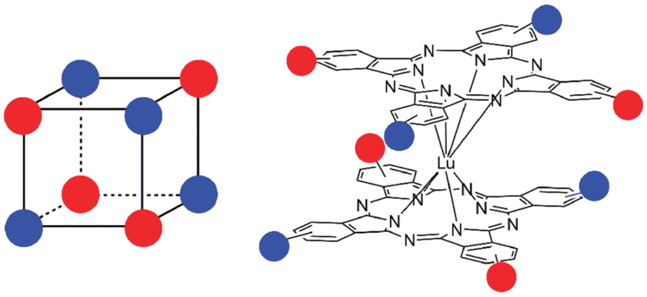

Figure 1. Bis(phthalocyanine)lutetium complex [Pc_2Lu] as a point-charge template for an octupole.

Such 3D delocalization between two cycles also exists in double-decker complexes that phthalocyanines (Pc) form with various ions, especially with lanthanide(III) ions,[4] and can approximate the electronic interactions along the edges of the cube. Electron spin resonance (ESR) studies of [Pc_2Lu] and theoretical calculations correlated to the observed absorption spectrum have shown that the molecule has an odd number of electrons and that the unpaired electron is completely delocalized over both rings, giving rise to a characteristic electronic transition in the near-IR region.[5] More interestingly, X-ray diffraction studies of [Pc_2Nd] and [Pc_2Lu] showed that

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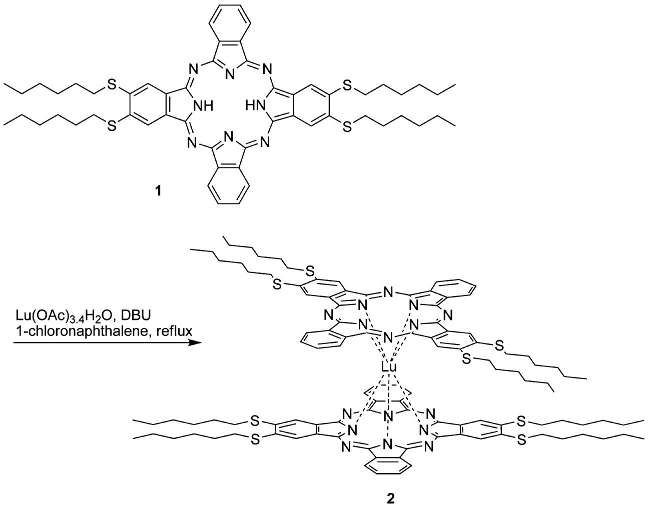
the two Pcs rings are rotated 45° with respect to each other,[6] giving a non-centrosymmetric structure of approximately D_{4d} symmetry. If one imagines lanthanide complexes with crosswise ABAB macrocycles featuring alternating electron-donor and electron-acceptor groups, an almost exact representation of the octupolar cube could be obtained (Figure 1), even if the symmetry is lowered to D_2, an unusual apolar chiral group. Because of their extended π-electron systems, phthalocyanines and their transition-metal complexes have been used to build up interesting nonlinear compounds, including various octupolar structures.[7] Surprisingly, intervalent bis(phthalocyaninato)lanthanide sandwich complexes have seldom been studied. Only their third-order nonlinear properties have been reported.[8] The most detailed study was reported by Shirk et al.,[8a] who investigated the cubic hyperpolarizabilities γ of a series of homoleptic simple [Pc_2Ln] complexes by degenerate four-wave mixing at 1064 nm. The measured hyperpolarizabilities γ were among the highest reported at this wavelength. The authors showed that the intervalence transition, which involves considerable charge transfer, does not have a dominant influence when it is not in resonance with the incident wavelength.

In this communication, we report on our first step toward the construction of a true octupolar cube using lanthanide complexes with crosswise ABAB macrocycles. A bis(phthalocyaninato)lutetium sandwich complex with a crosswise ABAB phthalocyanine bearing electron-donor (thioalkyl) groups on two opposite rings was synthesized and its first molecular hyperpolarizability β measured. Although there are no real electron-acceptor groups, the required ABAB-type alternation for one face of the cube is present, as thioalkyl groups and hydrogen atoms do not have the same electronic effect.

A large number of homoleptic and even heteroleptic lutetium sandwich complexes have been prepared with symmetrical A_4 phthalocyanines, usually by cyclic tetramerization of the corresponding phthalodinitriles in the presence of a lanthanide salt and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). This method could not be envisaged in our case, as a specific ABAB geometry is required for the two macrocycles. Therefore, the regioselective synthesis of the crosswise free base 2,3,16,17-tetra(hexylthio)phthalocyanine (**1**) (Scheme 1) was achieved using the coupling of 1,3,3-trichloroisoindolenine with 5,6-bis(hexylthio)-1,3-diiminoisoindoline (Scheme SI-1 in the Supporting Information).[9] The ABAB phthalocyanine was obtained as the major product, but significant amounts of 2,3,9,10,16,17-hexa(hexylthio)phthalocyanine (AB_3) and traces of the symmetric derivative 2,3,9,10,16,17,23,24-octa(hexylthio)phthalocyanine (B_4) were nevertheless produced, requiring thorough purification by chromatography. Finally, the bis(phthalocyaninato)lutetium complex **2** was obtained in good yield from the ABAB phthalocyanine and lutetium(III) acetate in refluxing 1-chloronaphthalene using DBU as a base (Scheme 1).[10]

Scheme 1. Synthesis of Complex 2



2 was crystallized from a concentrated chloroform solution by slow diffusion of methanol, and the crystal structure was resolved by X-ray diffraction.[11] The molecular central core has a structure very similar to that of the previously reported unsubstituted[6b] and octasubstituted[12] bis(phthalocyaninato)lutetium(III) complexes. Two phthalocyanine rings flank the central Lu^{3+} ion. As expected, there is a staggering angle (α) of 45° between the two cycles that creates a chiral noncentrosymmetric molecule (Figure 2a). The Lu^{3+} ion is octacoordinated by the eight nitrogen atoms of the isoindoles (N2 and N6, denoted as N_{iso}) in a slightly distorted square-antiprism geometry (Figure 2b). In Figure 2b, the N2 atoms (the N_{iso} atoms of the isoindole rings bearing the electron-accepting groups) and the N6 atoms (which bear the electron-donating groups) are pictured in different colors to show the parallel between the coordination polyhedron and the octupolar cube in Figure 1. The Lu−N_{iso} distances (2.356 and 2.366 Å) are slightly shorter than those reported for similar complexes [2.377−2.394 Å for the octa(hexylthio) analogue and 2.380 Å for Pc_2Lu]. The interplane distance between the two macrocycles, defined as the distance between the mean planes formed by the two sets of four N_{iso} atoms, is 2.656 Å, which is also shorter than the reported values (2.67−2.70 Å).[6b,12] In **2**, the two phthalocyanine rings are only slightly distorted from planarity, with a maximum of only 8.7° for the dihedral angle between the mean plane of the four N_{iso} atoms and the isoindole ring bearing the two thioalkyl chains. This small angle, combined with the short interplanar distance, gives hope for good electronic delocalization and good optical properties.

Figure 3 shows the absorption spectra of **1** and **2** in chloroform solution. **1** presents the classical spectrum of a low-symmetry phthalocyanine with a B band at 340 nm and an intense Q band split in two with maxima at 682 and 719 nm. Upon complexation, small hypsochromic shifts are observed for both the B and Q bands, with disappearance of the splitting. The substitution of the Pc ring with the four electron-donating thio(hexyl) groups provokes a red shift of all maxima relative to the unsubstitued analogues.[4] The main features of the electronic spectrum of **2** (Figure 3 inset) are a broad, intense absorption in the near-IR appearing between 1200 and 1600 nm and a sharp but weak band at 933 nm. This is characteristic of the intervalence band and corresponds to the $b_1 \rightarrow a_2$ excitation between the delocalized b_1 bonding molecular orbital (MO) and the a_2 antibonding MO.[13]

Nonpolarized harmonic light scattering (HLS; also named hyper-Rayleigh scattering)[14] experiments in chloroform were used to measure the dynamic molecular first hyperpolarizability, $\sqrt{\langle \beta_{HLS}^2 \rangle}_{1907}$ of **2**. The incident wavelength of 1907 nm is higher than the absorption cutoff and is therefore off-resonance

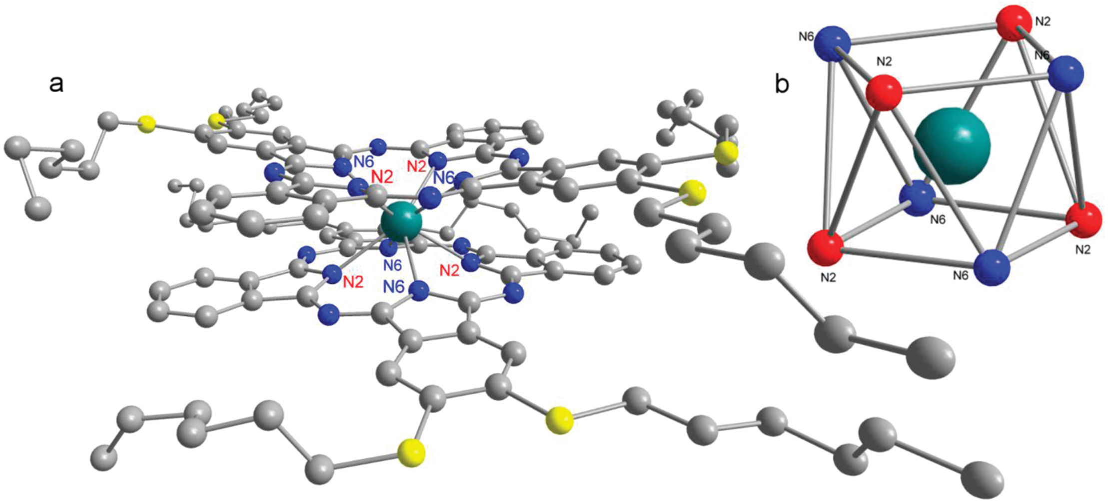


Figure 2. (a) X-ray crystal structure of **2** (H atoms and the solvent molecule have been omitted for clarity) and (b) coordination polyhedron around the Lu^{3+} ion.

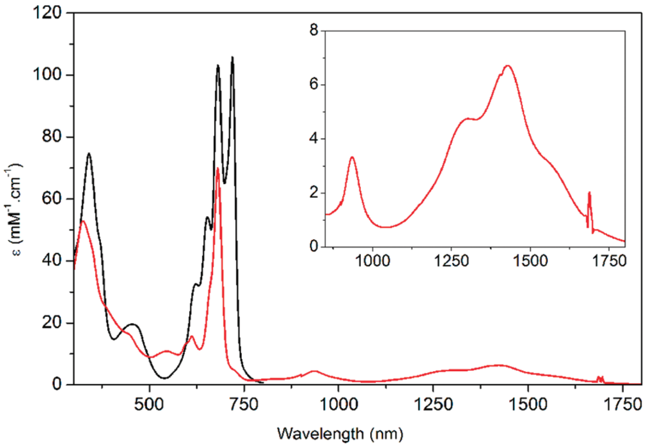


Figure 3. Absorption spectra of **1** (black) and **2** (red) in chloroform. The inset shows the NIR absorption of **2**.

with the intervalence band. It should be noted that the scattered light at the second harmonic (953 nm) is partially absorbed by the chromophore at the small sharp peak of the intervalence transition at 933 nm. A low concentration (10^{-5} M) was therefore used, and the HLS data were corrected for chromophore absorption before the determination of β. The first hyperpolarizability obtained was exceptionally large, with a value of 5750×10^{-30} esu for $\sqrt{\langle \beta_{HLS}^{2} \rangle}_{1907}$.[15,16] To the best of our knowledge, this is one of the highest values reported for a non-dipolar compound; it compares well to the very best octupolar chromophores described to date[17] and is much higher than the value for the paracyclophane derivative described by Bazan (46×10^{-30} esu).[3] The origin of the large second-order nonlinear response has not yet been investigated. At that wavelength, multilevel resonance enhancement cannot be ruled out.[18]

In summary, we have designed and obtained an efficient second-order octupole whose structure is probably the closest yet reported to the true octupolar cube and that displays an exceptionally large value of $\sqrt{\langle \beta_{HLS}^{2} \rangle}_{1907}$. This simple structure also offers interesting possibilities for easy variations. In particular, since the position of the intervalence band is directly related to the interplane distance, changing the central metal ion should change the optical properties by shifting the absorption further into the IR. Work in that direction has started. We have noticed that the lutetium complex presents the highest hyperpolarizability over the lanthanide series, even if for other ions the 1907 nm laser wavelength comes into resonance with the intervalence band. This seems to indicate that the intervalence transition has little influence on the quadratic nonlinear response, as was observed previously for third-order nonlinear properties.[8a] Calculations to explain this phenomenon are also in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, characterization, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(11) CCDC 832167 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.. Crystal data for $\mathbf{2}\cdot(CHCl_3)_2$: $C_{112}H_{128}LuN_{16}S_8\cdot 2(CHCl_3)$, black prism; orthorhombic, space group *Fddd* (No. 70); $a = 23.206(5)$ Å, $b = 29.202(2)$ Å, $c = 31.760(2)$ Å; $V = 21523(5)$ Å^3; $Z = 8$; $D_c = 1.452$ g cm^{-1}; $F_{000} = 9688$; Mo Kα radiation ($\lambda = 0.71070$ Å); $T = 100$ K; $\theta = 3.4–29.6°$; 28119 reflns collected, 6787 unique ($R_{int} = 0.078$); final GooF = 0.96; $R_1 = 0.059$, $wR_2 = 0.170$; R indices based on 5785 reflns with $I > 2\sigma(I)$ (refinement on F^2, 400 parameters).

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