

A Discrete Quadruple-Decker Phthalocyanine

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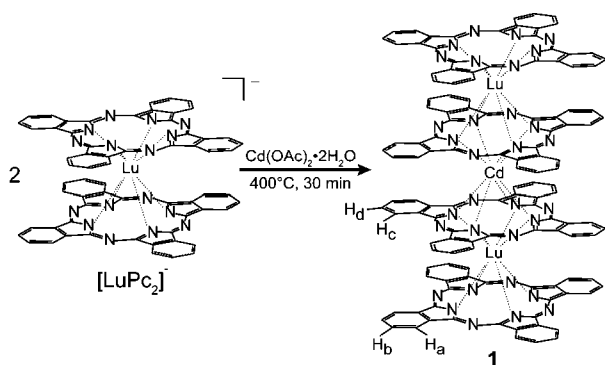
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The ability to form stacked sandwich-type phthalocyanine (Pc) oligomers in the presence of ions of metals such as lanthanides (Ln), yttrium, indium, and bismuth results in the formation of double- or triple-decker Pc complexes having unusual spectroscopic, electrochemical, and magnetic properties due to their π systems and/or f electrons.¹ The resulting complexes have therefore attracted considerable attention in various research fields, with a strong focus on their use as electrochromic materials² or single-molecule magnets (SMMs).³ No larger discrete stacked oligomer congeners have been reported to date, however, although mixtures of higher-order oligomeric species have been detected by mass spectrometry for mercury⁴ and cadmium⁵ complexes. Since the Pc ligand is a dianion [Pc(2-)] and lanthanide ions are present as trivalent cations (Ln^{III}), LnPc₂ formation results in an anionic species (the blue form) unless the complex is oxidized to form a neutral [LnPc₂]⁰ radical (the green form). In this sense, Ln₂Pc₃ can be regarded as the [LuPc₂]⁻ blue form coordinated by an [Ln^{III}Pc(2-)]⁺ species. It is clear on this basis that [LuPc₂]⁻ can potentially stack a second [LuPc₂]⁻ species through coordination with an appropriate central metal ion.

In this paper, we report the preparation of **1**, the first example of a discrete quadruple-decker Pc (Scheme 1). The Cd²⁺ ion was selected to form a neutral complex with two stacked [LuPc₂]⁻ units. Cook and co-workers have recently reported that Cd²⁺ has the ability to form sandwich-type Pc complexes.^{5,6} A mixture of an unsubstituted [LuPc₂]⁻[NBu₄]⁺ species⁷ and cadmium acetate [Cd(OAc)₂·2H₂O] was heated at 400 °C for 30 min under argon. Chromatographic separation of the resulting mixture gave **1** as a dark-purple powder in 3.4% yield (Scheme 1). See the Supporting Information (SI) for experimental details.

Scheme 1. Synthesis of **1**



A molecular-ion peak was observed at m/z 2512.3883 (calcd for **1**: m/z 2512.3873) in a high-resolution electrospray ionization Fourier transform ion cyclotron resonance (ESI-FTICR) mass measurement. Elemental analysis results were consistent with a neutral structure having no counterions (C 61.59, H 2.99, N 17.41;

calcd for C₁₂₈H₆₄N₃₂Lu₂Cd, C 61.19, H 2.57, N 17.84). The complex was stable in air at ambient temperatures in the solid state and moderately stable in solution for a couple of days. However, the complex tended to decompose to double-decker Pcs when CH₂Cl₂ or CHCl₃ solutions were allowed to stand for more than 1 week, making the growth of single crystals for X-ray crystallography problematic.

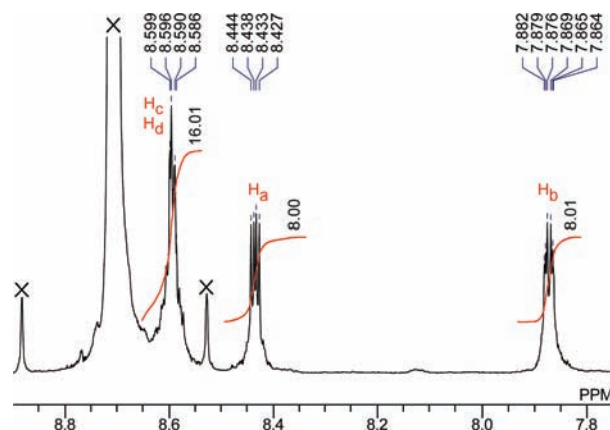


Figure 1. ¹H NMR spectrum of **1** in pyridine-*d*₅. Signals from the solvent are marked with ×.

A quadruple-decker structure contains distinct sets of outer and inner Pc ligands. The ¹H NMR spectrum of **1** (Figure 1) exhibits three sets of proton signals at 8.59, 8.43, and 7.87 ppm with an integration ratio of 2:1:1, respectively, indicating the presence of two nonequivalent types of Pc ligands. The ¹H–¹H COSY spectrum (see the SI) demonstrated that the latter two sets of protons are correlated with each other, while the signal at 8.59 ppm exhibits no correlation with any other protons. Since it is known that the ¹H signals of the inner Pc of triple-decker complexes lie at higher frequencies than those of the two outer Pc rings and that the signals of α protons typically appear at higher frequencies than those of β protons, the signals at 8.43 and 7.87 ppm can be assigned to the H_a and H_b protons of the outer Pcs, while the signal at 8.59 ppm can be assigned to the inner Pcs.^{5a,8} The nuclear Overhauser effect (NOE) experiment demonstrated that irradiation of the signal at 8.59 ppm induces NOEs in the other two signals, since the two nonequivalent Pcs lie in close proximity. There are seven distinct carbon signals at 160.62, 156.48, 137.33, 130.66, 129.33, 124.55, and 122.44 ppm in the ¹³C NMR spectrum. The eighth signal, which would be anticipated for a discrete quadruple-decker structure, is probably obscured by the solvent peaks (see the SI). The results of the ¹³C–¹H COSY and DEPT90 experiments were also found to be broadly consistent with this structure type (see the SI).

Figure 2 contains the absorption (bottom) and magnetic circular dichroism (MCD, top) spectra of **1** in CHCl₃. Three distinct absorption bands at 332, 623, and 727 nm were observed. The latter

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two peaks are shifted to longer wavelength relative to the spectrum of $[\text{LuPc}_2]^-$.⁹ Since the derivative-shaped signals observed in the MCD spectrum closely resemble the Faraday *A* terms observed for complexes with a threefold or higher axis of symmetry, the main $\pi\pi^*$ excited states either retain the orbital degeneracy of the corresponding Pc monomer states or have only relatively minor zero-field splittings. The spectra of **1** closely resemble those of the $[\text{LuPc}_2]^-$ blue form and Lu_2Pc_3 rather than those of the $[\text{LnPc}_2]^0$ green form, and all four Pc ligands can therefore be assigned a formal charge of 2-. The intensity ratio of the major bands in the 500–800 nm region is reduced from the value of 0.48 observed for $[\text{LuPc}_2]^-$ in CHCl_3 to 0.24. According to a theoretical approach developed by Ishikawa and co-workers,¹⁰ the spectral changes caused by the stacking of Pc monomers can be interpreted on the basis of exciton (EC) states generated by the excitation of a single ligand and charge resonance (CR) states generated by charge transfer between Pc rings. A lower-energy band with lower intensity typically arises from a transition with more CR character, while a more intense band at slightly higher energy arises primarily from an EC interaction. Since the electronic structure of **1** is broadly similar to that of $[\text{LuPc}_2]^-$, the bands observed at 623 and 727 nm can be assigned as Q bands arising from EC- and CR-dominated transitions, respectively.

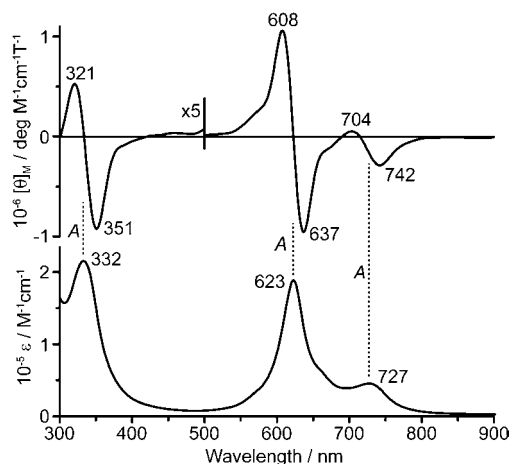


Figure 2. (bottom) Absorption and (top) MCD spectra of **1** in CHCl_3 .

The quadruple-decker structure of **1** undergoes four reversible one-electron oxidation steps ($E_{1/2} = -0.26, 0.05, 0.46,$ and 0.77 V vs Fc^+/Fc) and four reversible one-electron reduction steps ($E_{1/2} = -1.16, -1.49, -1.81,$ and -2.05 V) (Figure 3), while the corresponding cyclic voltammograms of $[\text{LuPc}_2]^-$ contain two oxidation and up to three reduction couples under the same conditions (see the SI). The gap between the first reduction and oxidation potentials is narrower in the case of **1**. This “stacking effect” has been reported previously for lutetium naphthalocyanine triple-decker and μ -oxo silicon Pc oligomers.^{11,12} The potential barrier for oxidation/reduction steps is decreased because the positively charged hole in the HOMO or electron in the LUMO introduced by the redox process is delocalized over all four Pc rings.

In summary, we have succeeded in synthesizing the first example of a discrete quadruple-decker Pc tetramer, **1**, through the reaction of $[\text{LuPc}_2]^-$ with cadmium acetate. The structure of **1** has been

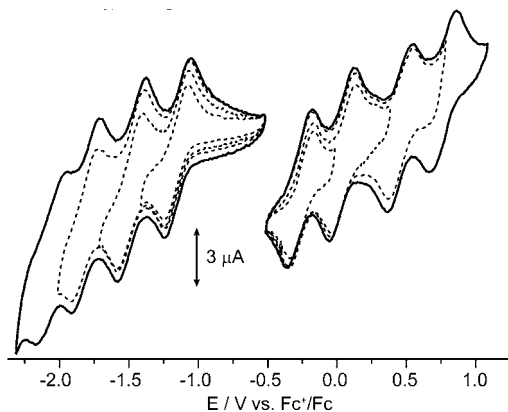


Figure 3. Cyclic voltammograms of **1** ($c = 1.0$ mM) in *o*-dichlorobenzene with 0.1 M tetrabutylammonium perchlorate. Sweep rate = 50 mV s^{-1} .

unambiguously established by high-resolution mass spectrometry, elemental analysis, and NMR spectroscopy. As anticipated, the optical spectra of **1** are broadly similar to those of $[\text{LuPc}_2]^-$. However, significant bathochromic shifts and a change in the intensity ratio of the EC- and CR-related Q bands are observed as a result of the formation of a multilayered oligomeric π structure. The electrochemical data also provide evidence for the stacking effects that would be anticipated for a quadruple-decker Pc complex. The synthesis of a wider range of tetramers is currently in progress, and their properties will be reported as a full paper in due course.

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Supporting Information Available: High-resolution mass spectrum; ^{13}C NMR, ^1H – ^1H COSY, ^{13}C – ^1H COSY, DEPT90, and NOE spectra; and spectroscopic and electrochemical data of the blue form. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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