Mixed Phthalocyaninato-Porphyrinato Europium(III) Triple-decker Sandwich Complexes Containing a Conjugated Dimeric Porphyrin Ligand

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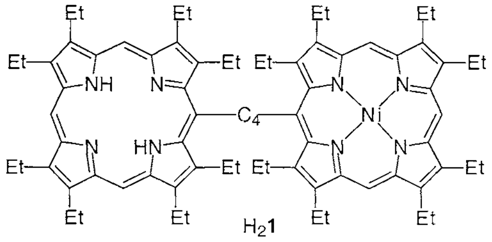
The first examples of triple-decker europium(III) sandwich complexes containing bis(octaethylporphyrinyl)butadiyne and phthalocyanine have been prepared by condensation of NiOEP-C_4-OEPH_2 (H_2**1**) and Li_2Pc with Eu(acac)$_3$·H_2O. The complexes (Pc)Eu(**1**)Eu(Pc) and (**1**)Eu(Pc)Eu(Pc) were characterized by NMR, IR, Raman, UV-vis, and mass spectra.

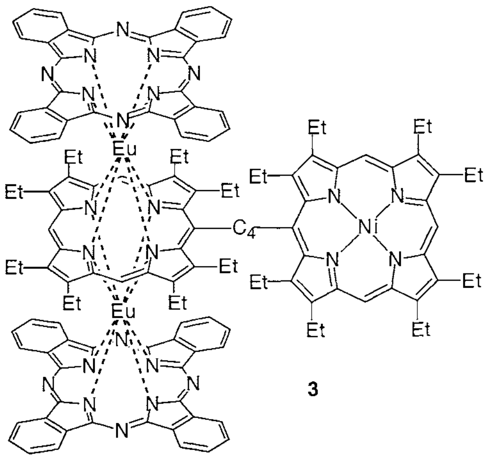
Diporphyrins linked by conjugated alkynes directly attached to the *meso* positions have unique spectroscopic properties indicative of strong inter-porphyrin communication in the ground and excited states.[1-4] One series of dimeric porphyrins studied by our group comprises homo- and heterobimetallic complexes of bis(octaethylporphyrinyl)butadiyne, H_2OEP-C_4-OEPH_2.[4] The homo- and heteroleptic double- and triple-decker complexes of rare earth metal ions with porphyrins and phthalocyanines (Pc) have evinced much interest lately because of the electronic interaction between the face-to-face aromatic macrocycles.[5] This renders them potentially useful in fields such as electrochromism, molecular semiconductors, magnets, and electronic components, chemical sensors, and non-linear optical materials. Given the wide interest in both conjugated porphyrin dimers and sandwich complexes, it appeared to be desirable to combine the attributes of these two structural types into the one molecule. Moreover, the presence of a covalently-linked dimeric ligand offers the intriguing possibility of forming "super-sandwiches" by complexation at both ends of the dimer.

In this letter, we describe the synthesis and spectra of the first examples of mixed (OEP dimer)-Pc-Eu(III) triple-decker sandwiches, using the mononickel ligand H_2**1**.[4] One ring was protected by coordination of Ni(II) to avoid (for our present purposes) double sandwich complexation of Eu(III) to the diporphyrin. Nickel(II) was chosen because it is not removed under the vigorous metallation conditions required for Eu(III), and its diamagnetism simplifies structural determination by NMR spectroscopy. As far as we are aware, this is the first isolation of sandwich complexes of a linear extended porphyrin dimer, although Lu and Ce sandwiches of face-to-face bridged dimers are known.[6]



H_2**1**

The synthesis followed the conventional metallation method used in the literature to prepare various heteroleptic tetraarylporphyrinato-Pc complexes and the OEP-Pc analogue.[7-9] Treatment of the mononickel ligand H_2**1** and Li_2Pc with an excess of Eu(acac)$_3$·H_2O in refluxing 1,2,4-trichlorobenzene for 12 h under a slow argon stream yielded a mixture of olive-green products. These were separated by column chromatography and further purified by chromatography and recrystallization, and proved to be triple-decker sandwiches with the stoichiometries Eu_2**1**$_2$Pc (**2**) and Eu_2**1**Pc_2 (**3**, **4**). The former species proved to be highly insoluble in common solvents once isolated from solution, and was characterized only by the presence of the appropriate molecular ion in its MALDI-TOF mass spectrum. It is expected to have the symmetrical structure **1**Eu(Pc)Eu**1**, by analogy with known Eu_2(Por)$_2$(Pc) complexes, including (OEP)Eu(Pc)Eu(OEP).[9]



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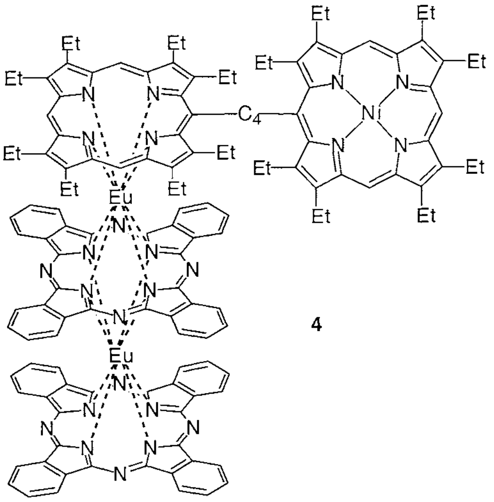

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The products **3** and **4** were recovered in yields of 33 and 17%, respectively. Compound **3** possesses the symmetrical structure (Pc)Eu(1)Eu(Pc), and compound **4** the unsymmetrical one (1)Eu(Pc)Eu(Pc), as shown by their ^{1}H NMR spectra.[10,11] This was easily assigned by consideration, *inter alia*, of the protons of the Pc rings, and the *meso* protons of the Eu-coordinated OEP ring. The former appear as two multiplets at 8.15 and 9.60 ppm for isomer **3**, and as two pairs of multiplets at 8.64, 10.08 ("outer" Pc ring) and 10.89, 12.66 ppm ("inner" Pc ring) for **4**. The *meso* protons resonate at 13.26 (1H) and 18.05 (2H) ppm for **3**, and at 9.18 (1H) and 14.42 (2H) ppm for **4**, and these shifts are as expected for additive effects of the paramagnetic Eu(III) ions. The *meso* proton resonances of the remote NiOEP ring appear as sharp singlets only slightly downfield from their positions in bis(NiOEP)butadiyne.[4]

The solid state Raman spectra (excited by a 633 nm laser) of compounds **3** and **4** confirmed the presence of the intact butadiyne bridge, by the characteristic strong bands at 2168 and 1462 cm^{-1}, shifted slightly from those for bis(NiOEP)butadiyne (2161, 1472 cm^{-1}).[4] In the IR spectrum, both isomers show the expected marker bands for coordinated Pc^{2-}, namely 1375 (w), 1329 (ms), and 1070 (s) cm^{-1}.[12]

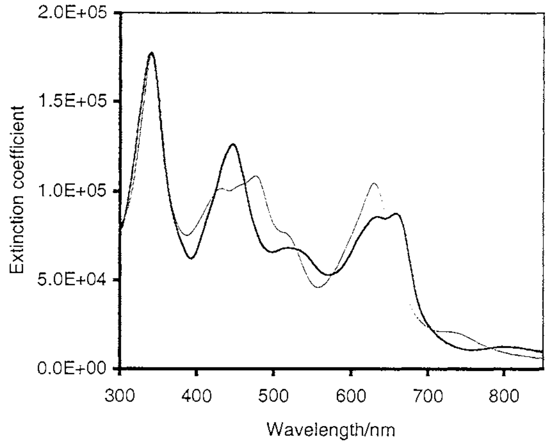

Figure 1. Electronic spectra of **3** (heavy line) and **4** (fine line).

Finally, the electronic absorption spectra confirm the presence of both OEP and Pc rings, and also exhibit bands indicating some inter-ring interaction (Figure 1). The band at 341 nm in both complexes is clearly the Pc Soret band, while the absorption between 400 and 550 nm is due mainly to the dimeric porphyrin ligand. In symmetrical isomer **3**, the region is dominated by a band at 447 nm, accompanied by a broad envelope between 500 and 550 nm. In contrast, the 400-500 nm region of the spectrum of **4** resembles more closely the typical appearance of this region for other bis(MOEP)butadiyne complexes, with three components visible.[4] The absorption in the >600 nm range is expected to comprise the Q bands of the Pc and OEP dimer ligands, and again the two spectra differ markedly in shape in this domain. Both isomers have very broad far-red bands at *ca.* 798 (**3**) and 730 (**4**) nm. A complete explanation of the origins of the interesting electronic spectra of bis(porphyrinyl)alkynes is presently lacking, despite a number of studies using different levels of empirical description and theory.[1,2,4,13,14] The additional complication of the presence of the Pc rings, and the likely existence of face-to-face interactions, mean that it is presently impossible to rationalize the interesting differences between the spectra of **3** and **4**. However, the original aim of our preliminary study has been realized, and we anticipate further developments in sandwich complexation of conjugated dimeric porphyrins.

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10 Data for **3**: ^{1}H NMR (CDCl$_3$, 300 MHz) Eu-OEP ring (paramagnetically broadened): 18.05, s, 2H; 13.26, s, 1H; 6.14, 2CH$_2$; 5.93, 2CH$_2$; 5.66, 2CH$_3$; 5.44, 2CH$_3$; 4.87, 2CH$_2$; *ca.* 4.4, 2CH$_2$ + 4CH$_3$; Pc rings: 9.60, m, 16H; 8.14, m, 16H; NiOEP ring: 9.85, s, 2H; 9.62, s, 1H; 5.58, *ca.* 4.4, 4.05, 4.00 (q, 2CH$_2$ each); 3.21, 2.30, 2.03, 1.95 (t, 2CH$_3$ each); UV-vis (CH$_2$Cl$_2$) λ_{max} (log ε) 341 (5.25), 447 (5.10), 518 br (4.83), 634 (4.93), 659 (4.94), 798 vbr (4.10) nm; MALDI-TOF MS (dithranol) cluster maximum 2498.8 (M$^+$ calcd. 2498.8); Found: C, 67.4; H, 4.8; N, 13.5%. Calcd. for $C_{140}H_{118}Eu_2N_{24}Ni$ C, 67.3; H, 4.8; N, 13.45%.

11 Data for **4**: ^{1}H NMR Eu-OEP ring: 14.42, s, 2H; 9.18, s, 1H; 4.98, *ca.* 4.1, 3.36, 3.13, 3.04, 2.40, 1.77 (m, diastereotopic CH$_2$); 1.46, 4CH$_3$; 1.20, 2CH$_3$; 0.54, 2CH$_3$; Pc rings: "inner" ring 12.66, 10.89, "outer" ring 10.08, 8.64 (m, 8H each); NiOEP ring: 9.84, s, 2H; 9.74, s, 1H; 4.83, 4.29, 4.08, 4.03 (q, 2CH$_2$ each); 2.37, 2.21, 2.05, 1.99 (t, 2CH$_3$ each); UV-vis (CH$_2$Cl$_2$) λ_{max} (log ε) 341 (5.25), 432 (5.00), 458 sh (5.02), 476 (5.04), 513 sh (4.89), 630 (5.02), *ca* 730 vbr sh (4.32); MALDI-TOF MS (dithranol) cluster maximum 2499.5 (M$^+$ calcd. 2498.8).

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