Synthesis and Spectroscopic Characterization of Heteroleptic Europium(III) Double-deckers Containing 2,3-Naphthalocyaninato and Tetra(4-pyridyl)porphyrinato Ligands

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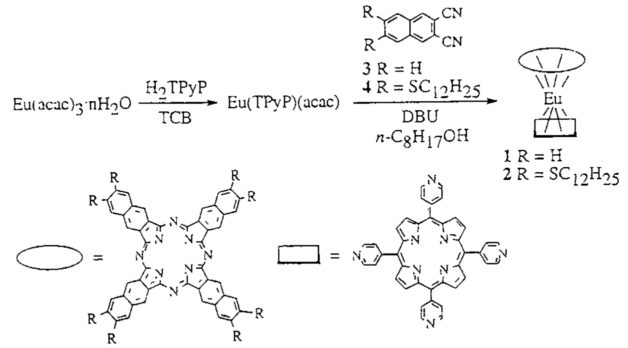
The first heteroleptic 2,3-naphthalocyaninato and porphyrinato double-decker complexes, namely Eu(Nc)(TPyP) (**1**) and Eu[Nc'$(SC_{12}H_{25})_8$](TPyP) (**2**), were prepared by the base-promoted cyclization of 2,3-dicyanonaphthalenes using Eu(TPyP)(acac) as the template, and were spectroscopically characterized.

Owing to the intriguing π-π interactions, sandwich-type phthalocyaninato (Pc) and porphyrinato (Por) metal complexes have attracted considerable attention in the recent literature.[1] The heteroleptic analogs containing mixed tetrapyrrole ligands are of particular interest because the individual chromophores can have very different optical and electrochemical nature which allows a detailed examination of their electronic structures and the extent of hole delocalization by various spectroscopic and electrochemical methods.[2] Although a substantial number of porphyrins have been incorporated into such mixed sandwiches, heteroleptic complexes having substituted Pc ligands are relatively rare.[3,4] 2,3-Naphthalocyanines are phthalocyanine's analogs with a more extended π system. It is expected that sandwich compounds having these macrocyclic ligands may exhibit distinct properties from those of the analogous Pc complexes. Naphthalocyaninato (Nc) sandwich compounds, however, have been little studied[5] and to our knowledge only one heteroleptic Nc complex, namely Lu(Nc)(Pc),[5a-f] has been reported so far, probably due to a synthetic barrier. We have recently developed an efficient route to prepare the mixed Pc and Por complexes. This method involves a cyclic tetramerization of dicyanobenzenes using M(ring)(acac) (M = Y, Eu; ring = Pc, Por; acac = acetylacetonate) as the template.[4] We describe herein an extension of this methodology to prepare the first heteroleptic Nc and Por complexes.

Treatment of 2,3-dicyanonaphthalene (**3**) with the half-sandwich complex Eu(TPyP)(acac), generated *in situ* from Eu$(acac)_3 \cdot nH_2O$ and the metal free tetra(pyridyl)porphyrin (H_2TPyP), in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave the mixed sandwich compound Eu(Nc)(TPyP) (**1**) in 52% yield. Compound **2** with eight thiolate side chains was prepared similarly starting from the dinitrile **4**.[6] Similar to the Pc analogs,[4b,c] the reactions yielded the protonated double-deckers EuH(Nc)(TPyP) and EuH[Nc'$(SC_{12}H_{25})_8$](TPyP) (Nc' = 3,4,12,13,21,22,30,31-octasubstituted naphthalocyaninate) as the initial products, which converted slowly in air to the corresponding one-electron ring-oxidized complexes. However, these protonated species, in particular, the latter which contains eight electron-donating dodecylthio side chains, were more susceptible to air oxidation than the Pc counterparts which may be related to the lower oxidation potential of Nc complexes.[5e,g] The conversion occurred during chromatographic purification and attempts to isolate pure samples of these species were not successful.



Compound **1** was characterized with MALDI-TOF mass spectroscopy using α-cyano-4-hydroxycinnamic acid as matrix. The spectrum showed intense signals centering at *m/z* 1482.4 assignable to the singly charged molecular ion. Distinct isotopic distribution could also be resolved which was found to be slightly deviated from the simulated spectrum of $[Eu(Nc)(TPyP)]^+$. This might be attributed to the co-existence of molecular ion (M^+) and protonated species (MH^+) which was observed previously for the Pc counterpart.[7] Compound **2** was also mass measured using L-SIMS technique with a 3-nitrobenzyl alcohol matrix. The isotopic cluster for the protonated molecular ion appeared at *m/z* 3084.6 (calcd. for MH^+ 3084.6).

The UV-Vis and near-IR spectra of **1** (Figure 1) are closely related to those of single-hole complexes $M^{III}[ring(1)^{2-}][ring(2)^{\bullet -}]$ and can be assigned in a similar manner.[2,4,8] By comparing with the data of Eu(Pc)(TPyP) (Table 1),[8] the TPyP Soret band (416 nm) and the visible π-radical anion ($ring^{\bullet -}$) band (488 nm) of **1** are red-shifted, while the Pc and Nc Soret bands (324 nm) appear at the same position. The lower-energy near-IR band (1084 nm), which can be attributed to an intramolecular ring-to-ring charge transfer transition, exhibits a substantial hypsochromic shift in **1**. A remarkable feature of **1** is the relatively intense Q band absorption peaking at 630 nm which is

Table 1. UV-Vis and near-IR data for **1**, **2** and Eu(Pc)(TPyP) in $CHCl_3$

Compound	λ_{max} / nm
1	324, 416, 488, 630, 893, 1084
2	317, 352, 419, 497, 659, 899, 1094
Eu(Pc)(TPyP)[8]	324, 403, 467, 978, 1218

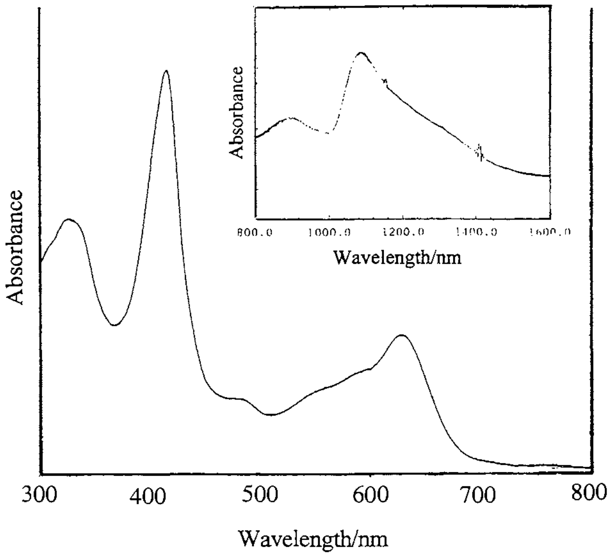


Figure 1. UV-Vis and near-IR (inset) spectra of Eu(Nc)(TPyP) (**1**) in $CHCl_3$.

almost invisible for the Pc analog. Compound **2** displays similar spectral features except that the Nc Soret band is split as in the case of substituted Pc complexes,[3a,4,9] and the Q band now becomes less intense. These data are summarized in Table 1.

The assignment was supported by the spectral changes of **1** and **2** in $CHCl_3$ / ethanol (3:1) upon addition of KBH_4, which acts as a reducing agent. Upon reduction, both the Nc and TPyP Soret bands were red-shifted by 1-3 and 6-8 nm, respectively, while a relatively intense absorption at 708 (for **1**) or 714 nm (for **2**) emerged which could be attributed to the Nc Q band. As expected, the characteristic near-IR band disappeared for both complexes showing that these single-hole species underwent one-electron reduction.

IR spectroscopy is a versatile tool in analyzing the extent of hole delocalization in single-hole complexes.[1a,2,8,10,11] The IR spectra of **1** and **2** exhibited a strong band at 1323 and 1321 cm^{-1}, respectively, which was shown as a diagnostic band for phthalocyanine π radical anion ($Pc^{\bullet -}$).[10] As the spectra did not show marker band for TPyP π radical anion ($TPyP^{\bullet -}$), which is supposed to appear at roughly the same position of tetraphenylporphyrin π radical anion (*ca.* 1270-1295 cm^{-1})[11] because of their similar skeleton, it indicated that the hole in **1** and **2**, similar to the case of Pc^- analogs,[4b,c,11] more likely resides on the Nc macrocycles. This is consistent with the theoretical calculations showing that H_2Nc has a higher HOMO level than H_2Pc,[12] and is also in accord with the hypsochromic shift of the near-IR band that can be ascribed to a $TPyP^{2-}$ to $Nc^{\bullet -}$ transition.

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6 Preparation of **1** and **2**: A mixture of $Eu(acac)_3 \cdot nH_2O$ (22 mg, 0.05 mmol) and H_2TPyP (34 mg, 0.06 mmol) in 1,2,4-trichlorobenzene (TCB) (4 ml) was allowed to reflux under nitrogen for 6 h. After being cooled, the mixture was evaporated under reduced pressure. Dinitriles **3** or **4** (0.22 mmol), DBU (50 mg, 0.33 mmol) and *n*-octanol (4 ml) were then added and the mixture was refluxed for a further 8 (for **1**) or 18 h (for **2**). The volatiles were then removed *in vacuo* and the residue was subjected to column chromatography using $CHCl_3$ / MeOH (100:1) (for **1**) or $CHCl_3$ (for **2**) as eluent. Compound **1** was further purified by repeated chromatography and recrystallization from $CHCl_3$ / MeOH (5:1) as a black solid (52%). Compound **2** was isolated as a greenish-brown solid in 69% yield.

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