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Investigation of Rational Syntheses of Heteroleptic Porphyrinic Lanthanide (Europium, Cerium) Triple-Decker Sandwich Complexes

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The use of lanthanide triple-decker sandwich molecules containing porphyrins and phthalocyanines in molecular information storage applications requires the ability to attach monomeric triple deckers or arrays of triple deckers to electroactive surfaces. Such applications are limited by existing methods for preparing triple deckers. The reaction of a lanthanide porphyrin half-sandwich complex ((Por)M(acac)) with a dilithium phthalocyanine ($PcLi_2$) in refluxing 1,2,4-trichlorobenzene (bp 214 °C) affords a mixture of triple deckers of composition (Pc)M(Pc)M-(Por), (Por)M(Pc)M(Por), and (Pc)M(Por)M(Pc). We have investigated more directed methods for preparing triple deckers of a given type with distinct metals in each layer. Application of the method of Weiss, which employs reaction of a (Por)M(acac) species with a lanthanide double decker in refluxing 1,2,4-trichlorobenzene, afforded the desired triple decker in some cases but a mixture of triple deckers in others. The approach we developed employs in situ formation of the lanthanide reagent $EuCl[N(SiMe_3)_2]_2$ or $CeI[N(SiMe_3)_2]_2$, which upon reaction with a porphyrin affords the half-sandwich complex (Por)EuX or (Por)CeX′ ($X = Cl$, $N(SiMe_3)_2$; $X' = I$, $N(SiMe_3)_2$). Subsequent reaction with $PcLi_2$ gives the double decker (Por)M(Pc). The (Por^1)EuX half-sandwich complex gave the desired triple decker upon reaction with (Pc)Eu(Pc) but little of the desired product upon reaction with (Por^2)Eu(Pc). The (Por^1)CeX′ half-sandwich complex reacted with europium double deckers (e.g., (tBPc)-Eu(Por^2), $(tBPc)_2Eu$) to give the triple deckers (Por^1)Ce(tBPc)Eu(Por^2) and (Por^1)Ce(tBPc)Eu(tBPc) in a rational manner (tB = tetra-*tert*-butyl). The reactions yielding the half-sandwich, double-decker, and triple-decker complexes were performed in refluxing bis(2-methoxyethyl) ether (bp 162 °C). The porphyrins incorporated in the various triple deckers include *meso*-tetrapentylporphyrin, *meso*-tetra-*p*-tolylporphyrin, octaethylporphyrin, and *meso*-tetraarylporphyrins bearing iodo, ethynyl, or iodo and ethynyl substituents. The triple deckers bearing iodo and/or ethynyl substituents constitute useful building blocks for information storage applications.

Introduction

The storage of information at the molecular level may afford extraordinarily high memory densities. We have developed an approach toward molecular-based information storage that involves the storage of data in distinct molecular oxidation states.[1−7] Thiol-derivatized redox-active molecules are attached to an electroactive surface, thereby enabling reading and writing to be achieved via electrical methods.[8] In principle, the information storage density can be increased commensurate with the number of available oxidation states of the molecules in a memory storage location. Among the various classes of molecules examined for information storage,[2−6] triple-decker lanthanide sandwich molecules[9,10] comprised of porphyrinic ligands proved most attractive due to their large number of redox states, reversible electrochemistry, and relatively low oxidation potentials. The triple deckers generally exhibit four oxidation states in the range 0−1.4 V (vs Ag/Ag^+), corresponding to the formation of the monocation, dication, trication, and tetracation. A further attraction of this class of molecules stems from the possibility of interleaving the potentials of two triple deckers, thereby achieving as many as eight accessible cationic oxidation states.[7] This approach for molecular-information storage requires the ability to synthesize triple deckers of a given type bearing linkers for attachment to an electroactive surface.

The synthesis of homoleptic porphyrin triple deckers, first reported by Buchler,[11] employed the reaction of an (acac)-lanthanide complex with a porphyrin in refluxing 1,2,4-trichlorobenzene.[12] This procedure grew out of a method developed by Horrocks[13] for the preparation of (porphyrin)·M(acac) complexes by reaction of a porphyrin with an

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(acac)$_3$lanthanide complex in refluxing 1,2,4-trichlorobenzene.[14] The synthesis of heteroleptic (porphyrin/phthalocyanine) triple deckers has been achieved by two distinct procedures: an undirected "reaction-of-monomers" route and a directed "monomer + dimer" route (vide infra). The reaction-of-monomers route proceeds as follows: a porphyrin is treated with excess $M(acac)_3 \cdot nH_2O$ in refluxing 1,2,4-trichlorobenzene,[12] affording the (porphyrin)·M(acac) complex.[15] The mixture is then treated with a dilithium phthalocyanine under continued reflux. In various applications of this method it has become clear that the product composition depends on the lanthanide, the nature of the substituents on the porphyrin and phthalocyanine, and the ratio of the reactants.[10] In our hands, the "reaction-of-monomers" route using M = Eu afforded two double deckers of composition (Por)M(Pc) and (Pc)M(Pc) and three triple-decker complexes of composition (Por)M(Pc)M(Por), (Pc)M(Por)M(Pc), and (Pc)M(Pc)M(Por);[16] the yields of the three types of triple deckers were typically 10−20%, ≤3%, and 10−14%, respectively, upon chromatographic purification.[6]

We elected to employ the (Pc)Eu(Pc)Eu(Por) type of triple decker for attachment via a thiol linker to an electroactive surface. The reasons were 2-fold. (1) We sought only one thiol linker per triple decker in order to avoid the complications that might arise with rotational isomers if two linkers were present. Rotational isomers have been reported in a cerium double decker containing two different porphyrins.[17] (2) The synthetic chemistry of porphyrins is better developed than that of phthalocyanines.[18] Thus, a synthetic handle in triple deckers would be more easily introduced via a suitably functionalized porphyrin monomer than with a phthalocyanine. This work led to a handful of thiol-derivatized (Pc)Eu(Pc)Eu(Por) triple deckers, which yielded self-assembled monolayers on gold electrodes with electrochemical properties suitable for molecular-based information storage.[6,7]

We also examined the solution electrochemical properties of the three types of triple deckers with a variety of substituted (but not thiol-derivatized) porphyrin and phthalocyanine rings.[7] The motivation for this work was to identify suitable pairs of triple deckers that exhibit interleaving of oxidation potentials, thereby affording the opportunity for increased density of information storage. In a number of cases, the triple decker of type (Por)Eu(Pc)Eu(Por) constituted one or both members of the pair of triple deckers. Triple deckers of type (Por^1)M(Pc)M(Por^2) are not readily available via the "reaction-of-monomers" synthesis. To minimize the arduous chromatography associated with the preparation of triple deckers of the type (Pc)Eu(Pc)Eu(Por) which we have worked with extensively, and to gain access to triple deckers of type (Por^1)Eu(Pc)Eu(Por^2) in which only one porphyrin bears a thiol linker, we investigated directed "monomer + dimer" syntheses of triple-decker compounds.

A directed synthesis of heteroleptic heteronuclear triple deckers has been described by Weiss's group.[19] The reaction of a (Por^1)M^1(acac) half-sandwich complex (M^1 = Gd, Lu, Y) and the double decker (Por^2)M^2(Pc) (M^2 = La, Ce) in refluxing 1,2,4-trichlorobenzene afforded triple deckers of the type (Por^1)M^1(Pc)M^2(Por^2) in high yields (64−81%) with no other triple deckers reported.[19] This "monomer + dimer" method has rarely been used. In one application, ^{u}PcLi$_2$, M(acac)$_3$, and (Pc^1)M(Pc^1) were reacted in refluxing 1,2,4-trichlorobenzene. In all cases examined, a mixture of (^{u}Pc)M(Pc^1)M(Pc^1) and (^{u}Pc)M(Pc^1)M(^{u}Pc) was obtained.[20] To our knowledge, the Weiss method has not been applied with a (Pc)M(Pc) double decker to obtain the (Pc)Eu(Pc)Eu(Por) triple decker. We began our studies by applying the Weiss method in pursuit of the (Pc)Eu(Pc)Eu(Por) or (Por^1)Eu(Pc)Eu(Por^2) complexes. We obtained a single triple decker with this method in some applications but mixtures of triple deckers in other applications. The mixtures of triple deckers likely result from cleavage of the double decker under the high-temperature conditions of the synthesis. Such limitations in scope prompted us to investigate rational routes that proceed at lower temperature for the synthesis of heteroleptic triple deckers.

In this paper, we first describe our results obtained upon application of the "monomer + dimer" method of Weiss. We then describe our studies aimed at developing new synthetic methods for the preparation of triple-decker compounds. The method we developed employs a reactive, non-acac lanthanide reagent that is formed in situ; the reaction of this complex with a porphyrin affords the half-sandwich complex. The reaction of the latter with a double decker affords the corresponding triple decker. Several triple deckers of the types (Por^1)M^1(Pc)M^2(Por^2) and (Pc)M^1(Pc)M^2(Por) have been prepared in this manner, where M^1, M^2 = Eu, Ce. Among the lanthanides, cerium is particularly attractive because cerium triple deckers exhibit metal-centered oxidation states in addition to the four ligand-centered cationic oxidation states.[21] The investigation of the information-storage properties of these compounds will be described elsewhere.

Results and Discussion

The porphyrins and phthalocyanines employed herein are shown in Chart 1. In the presentation, each double decker incorporating europium is assumed to be a radical species (not displayed in the nomenclature) unless specified otherwise. The double deckers incorporating cerium, and all triple deckers, are closed-shell species.

I. Synthesis of Triple Deckers using $Eu(acac)_3 \cdot nH_2O$. The Weiss method for preparing triple deckers of the type (Por^1)M^1(Pc)M^2(Por^2) proceeds as follows.[19] A porphyrin is treated with excess M^1(acac)$_3 \cdot n$H$_2$O in refluxing 1,2,4-trichlorobenzene[12] for 4 h, affording the (Por^1)M^1(acac) complex. This complex is treated with the mixed double-decker species (Por^2)M^2(Pc), and refluxing is continued for 8 h. Our efforts to prepare triple deckers of the types (Pc)Eu(Pc)Eu(Por) and (Por^1)Eu(Pc)Eu(Por^2) by applying this method are described below.

Reaction of (Por)Eu(acac) with (Pc)Eu(Pc). Treatment of TTPH$_2$ with excess $Eu(acac)_3 \cdot nH_2O$ in refluxing 1,2,4-tri-

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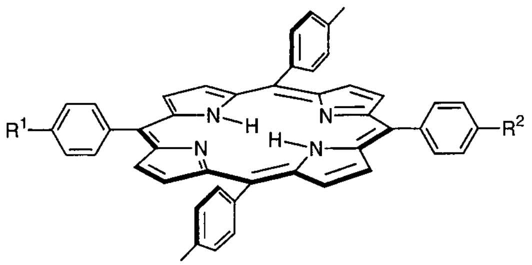
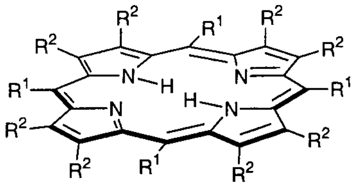
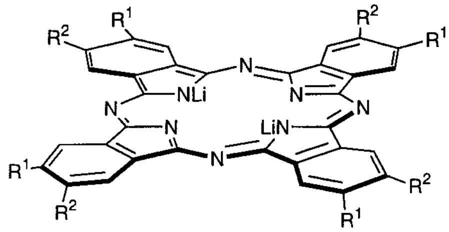
Chart 1



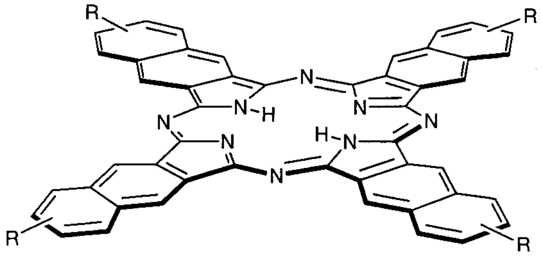
R^1 = R^2 = I	**1-PorH$_2$**
R^1 = TMS-ethynyl; R^2 = TIPS-ethynyl	**2-PorH$_2$**
R^1 = TMS-ethynyl; R^2 = I	**3-PorH$_2$**



R^1 = CH$_3$-C$_6$H$_4$/ R^2= H	**TTPH$_2$**
R^1 = C$_6$H$_5$/ R^2= H	**TPPH$_2$**
R^1 = pentyl/ R^2= H	**PnPH$_2$**
R^1 = H/ R^2= C$_2$H$_5$	**OEPH$_2$**



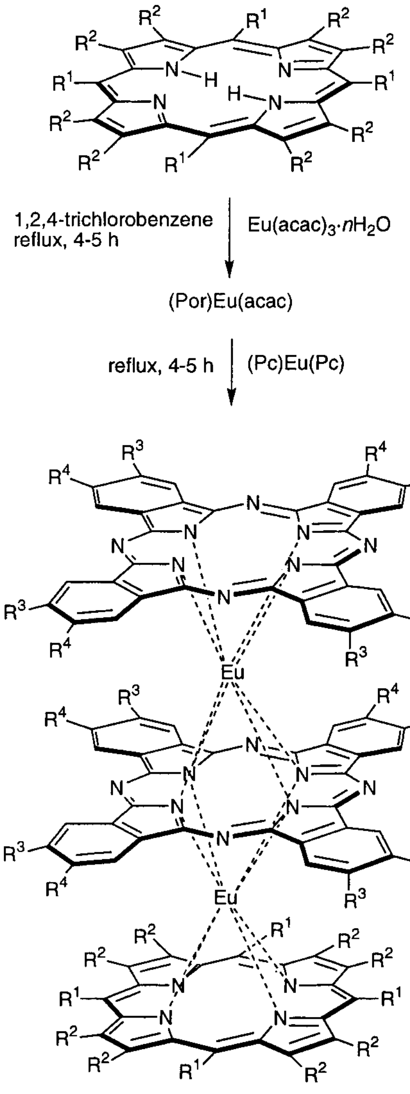
R^1 = R^2 = H	**^{u}PcLi$_2$**
R^1 = R^2 = octyloxy	**(octyloxy)$_8$PcLi$_2$**
R^1/R^2 = H; (CH$_3$)$_3$C	**tBPcLi$_2$**
R^1 = R^2 = heptyl	**(heptyl)$_8$PcLi$_2$**



R = H	**NcH$_2$**
R = *t*-Bu	**tBNcH$_2$**

chlorobenzene afforded the corresponding (TTP)Eu(acac) half-sandwich complex. Treatment of the latter with the unsubstituted (^{u}Pc)$_2$Eu double decker (vide infra) gave the expected triple decker (TTP)Eu(^{u}Pc)Eu(^{u}Pc) in 24% yield accompanied by unreacted starting materials (Scheme 1). The low yield may stem in part from the low solubility of the double-decker and triple-decker complexes, which caused difficulties in the chromatographic separation. Nonetheless, these results show that the Weiss "monomer + dimer" method could be applied with a

Scheme 1



(Por)Eu(Pc)Eu(Pc)

(TTP)Eu(^{u}Pc)Eu(^{u}Pc)	24%
(OEP)Eu(tBPc)Eu(tBPc)	76%
(**1**-Por)Eu(tBPc)Eu(tBPc)	69%
(**2**-Por)Eu(tBPc)Eu(tBPc)	75%

bis(phthalocyanine) double decker to obtain the expected triple decker (TTP)Eu(^{u}Pc)Eu(^{u}Pc) in a rational manner.

The use of tetra-*tert*-butylphthalocyanine (consisting of a mixture of regioisomers) for the preparation of triple deckers was found to improve the solubility of the sandwich complexes. The reaction of 5,15-bis(4-iodophenyl)-10,20-di-*p*-tolylporphyrin (**1**-PorH$_2$)[22] with Eu(acac)$_3$·nH$_2$O followed by the (tBPc)$_2$Eu double decker (vide infra) in 1,2,4-trichlorobenzene gave the triple decker (**1**-Por)Eu(tBPc)Eu(tBPc) in 69% yield. Similarly, the reaction of 5-[4-[2-(trimethylsilyl)ethynyl]phenyl]-15-[4-[2-(triisopropylsilyl)ethynyl]phenyl]-10,20-di-*p*-tolylporphyrin (**2**-PorH$_2$)[22] or octaethylporphyrin (OEPH$_2$) gave the triple decker (**2**-Por)Eu(tBPc)Eu(tBPc) in 75% yield or the triple decker (OEP)Eu(tBPc)Eu(tBPc) in 76% yield, respectively (Scheme 1). In each case, no other triple decker was observed. Thus, higher yields were obtained with the more soluble double decker

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[22] Schweikart, K. H.; Lindsey, J. S., unpublished results.

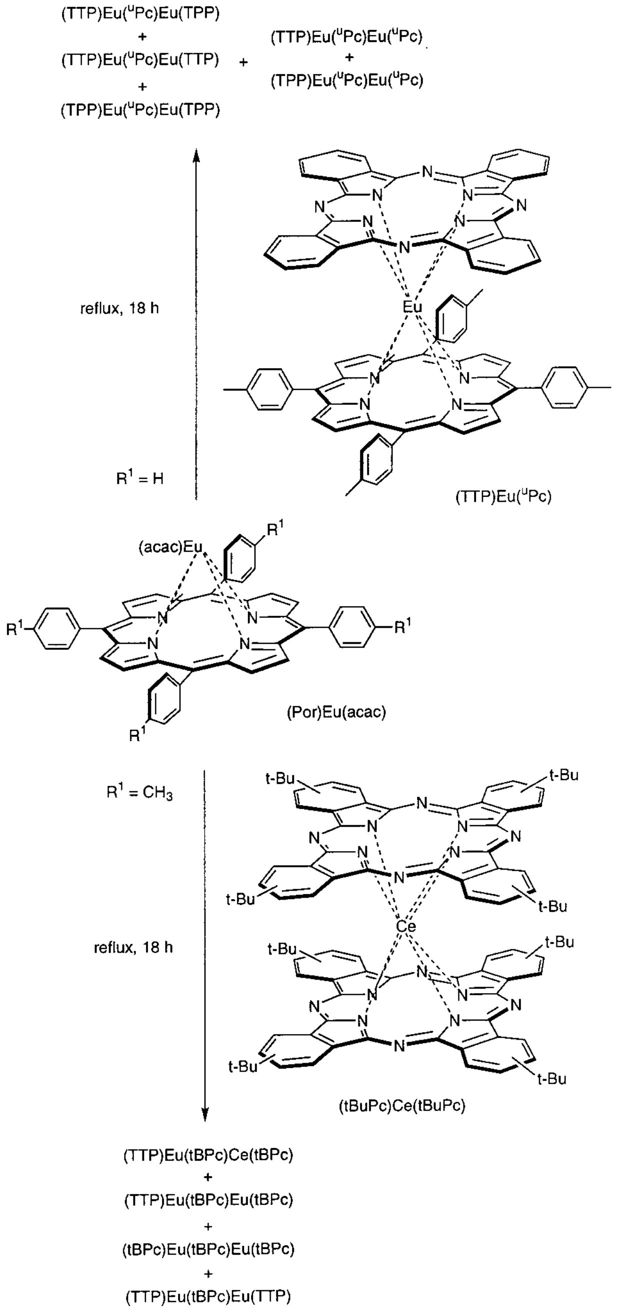
(tBPc)$_2$Eu than with (^{u}Pc)$_2$Eu. The triple deckers with iodo or ethyne substituents are valuable building blocks. The reaction of (TTP)Eu(acac) with the phthalocyanine double decker [(heptyl)$_8$Pc]$_2$Eu (vide infra) proved to be unsuccessful. This result may stem from steric congestion of the alkyl groups on the periphery of the phthalocyanine in the expected triple decker. Indeed, the reaction of (heptyl)$_8$PcLi$_2$ and octaethylporphyrin under the standard "reaction-of-monomers" conditions afforded exclusively the triple decker of type [(heptyl)$_8$Pc]Eu(Por)Eu[(heptyl)$_8$Pc].[7]

Each triple-decker complex was characterized by TLC, LD-MS, FAB-MS, UV−vis spectroscopy, and ^{1}H NMR spectroscopy. However, ^{1}H NMR spectroscopy was not particularly useful for the characterization of complexes containing the tetra-*tert*-butylphthalocyanine ligand due to the presence of phthalocyanine regioisomers.[23,24]

Reaction of (TPP)Eu(acac) with (TTP)Eu(^{u}Pc). Treatment of TPPH$_2$ with excess Eu(acac)$_3$·nH$_2$O in refluxing 1,2,4-trichlorobenzene afforded the corresponding (TPP)Eu(acac) half-sandwich complex. Treatment of the latter with (TTP)Eu(^{u}Pc) (vide infra) and further refluxing afforded a mixture of the three possible triple deckers of type (Por)Eu(^{u}Pc)Eu(Por): in other words, a mixture of (Por^1)Eu(^{u}Pc)Eu(Por^1), (Por^1)Eu(^{u}Pc)Eu(Por^2), and (Por^2)Eu(^{u}Pc)Eu(Por^2) as shown in Scheme 2. The presence of the components in the mixture was observed by LD-MS and ^{1}H NMR spectroscopy. Such a mixture suggests cleavage of the starting double decker prior to the formation of the triple-decker complexes.[25] Traces of the triple deckers (Por^1)Eu(^{u}Pc)Eu(^{u}Pc) and (Por^2)Eu(^{u}Pc)Eu(^{u}Pc) were also found in the mixture, which also reflects cleavage of the double decker. The separation of the mixtures of triple deckers of the same type was not possible, due to the similarities of the substituents in the porphyrins TTPH$_2$ and TPPH$_2$.

Reaction of (TTP)Eu(acac) with (tBPc)Ce(tBPc). Treatment of TTPH$_2$ with excess Eu(acac)$_3$·nH$_2$O in refluxing 1,2,4-trichlorobenzene afforded the corresponding (TTP)Eu(acac) half-sandwich complex. Treatment of the latter with the double decker (tBPc)Ce(tBPc) (vide infra) and further refluxing afforded a mixture of several triple deckers, including (TTP)-Eu(tBPc)Ce(tBPc) (main product in the crude mixture), (TTP)Eu(tBPc)Eu(tBPc), (tBPc)Eu(tBPc)Eu(tBPc) and (TTP)Eu(tBPc)-Eu(TTP) as shown in Scheme 2. The presence of the components in the mixture was observed by LD-MS. Such a mixture suggests cleavage of the starting double decker prior to the formation of the triple-decker complexes.[25,26] Chromatographic separation of the expected (tBPc)Ce(tBPc)Eu(TTP) triple decker and the undesired (tBPc)Eu(tBPc)Eu(TTP) was not possible.

Scheme 2



II. Investigation of Replacements for Eu(acac)$_3$·nH$_2$O. To find milder reaction conditions that could be used in the preparation of triple deckers, thereby avoiding the scrambling observed in some applications of the Weiss method, we sought lanthanide precursors in place of Eu(acac)$_3$·nH$_2$O that could be reacted at lower temperatures. Our first experiments focused on the europium salts EuCl$_3$, EuI$_2$, Eu(OTf)$_3$, Eu(acac)$_3$·nH$_2$O, and Eu(2,2,6,6-tetramethyl-3,5-heptanedionate)$_3$. These salts were used in metalation reactions with the porphyrins TTPH$_2$ and TPPH$_2$ in various solvents (DMF, THF, DME, bis(2-methoxyethyl) ether) as well as with different bases (DBU, 2,6-lutidine) under reflux conditions. The presence of metalated porphyrin was readily detected by UV−vis spectroscopy. In some cases partial metalation of the porphyrin occurred but the subsequent reaction with ^{u}PcLi$_2$ for preparing the desired sandwich complex did not give a clean product distribution.

To obtain the clean formation of a europium porphyrin half-sandwich complex that was stable in solution, we tried to

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(25) Double deckers are known to undergo cleavage. Indeed, Buchler's "raise-by-one-story" synthesis employs reaction of (Por)M(Por) alone to give the triple decker (Por)M(Por)M(Por).[26] Phthalocyanine-containing double deckers also undergo cleavage, as shown by the mixture of products obtained upon application of the Weiss "monomer + dimer" synthesis method by Liu et al.[20] We performed a control experiment to determine whether such scrambling results from the cleavage of the starting double decker or from rearrangement of a triple-decker product. A sample of (TTP)Eu(^{u}Pc)Eu(^{u}Pc)[6] was heated under the conditions of the Weiss method (excess Eu(acac)$_3$ in refluxing 1,2,4-trichlorobenzene) for 22 h. No scrambling was observed; however, we observed the slow decomposition of the triple decker, yielding TTPH$_2$ and (^{u}Pc)Eu(^{u}Pc).

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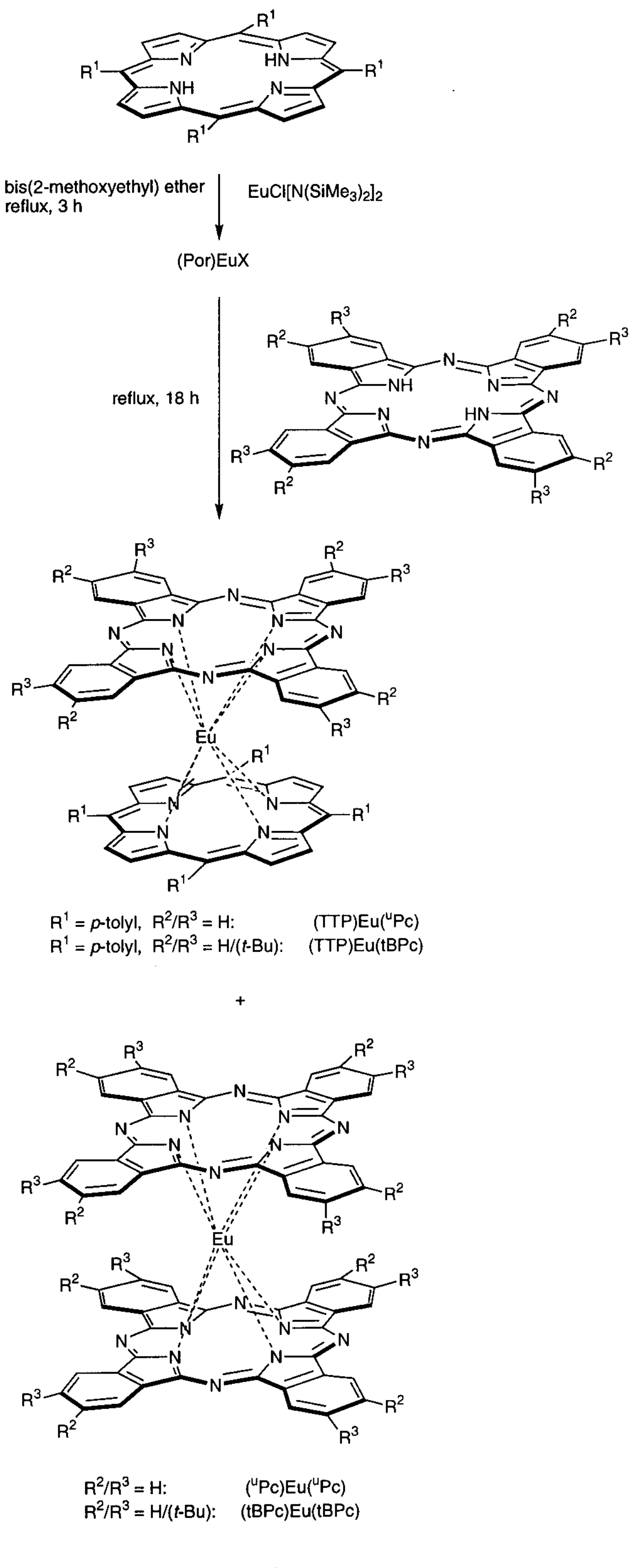
substitute the ligands on the europium center by organic substituents through reaction of EuX_3 (X = Cl, OTf, acac, 2,2,6,6-tetramethyl-3,5-heptanedionate) with RLi (R = *tert*-butyl, butyl, $Si(SiMe_3)_3$, $N(SiMe_3)_2$) in bis(2-methoxyethyl) ether. The only known compounds related to these experiments are $EuCl[N(SiMe_3)_2]_2$ [27] and $Eu[N(SiMe_3)_2]_3$.[28] The latter type of complex, $Ln[N(SiMe_3)_2]_3$ where Ln = Y, Yb, Er, was used for metalation of porphyrins by Wong et al.[29] Of the various RLi reagents that we examined, facile metalation yielding a europium porphyrin half-sandwich complex was obtained by using 2 molar equiv of the amide ligand (R = $N(SiMe_3)_2$) in reaction with $EuCl_3$ as described by Aspinall et al.[27] The process for preparation of $EuCl[N(SiMe_3)_2]_2$ and reaction with a free base porphyrin employed the following steps: (1) slow addition of 2 molar equiv of $LiN(SiMe_3)_2$ in THF to a vigorously stirred suspension of $EuCl_3$ in bis(2-methoxyethyl) ether at 0 °C, (2) warming to room temperature (1 h) and then stirring for 1 h, (3) addition of the porphyrin, and (4) refluxing the mixture for 3 h. In this manner, a stable solution of the europium porphyrin half-sandwich complex was obtained, as evidenced by UV−vis spectroscopy.[30] The half-sandwich complex, formulated as (Por)EuX where X = Cl, $N(SiMe_3)_2$,[31] is shown in Scheme 3. Note that additional solvent and/or salt molecules may be coordinated to the europium center. An X-ray study on crystals grown from a toluene solution of metalated *meso*-tetra-*p*-tolylporphyrin failed because of lack of reflections. The (Por)EuX half-sandwich complex is expected to react with a dilithium phthalocyanine to give sandwich complexes.[31] This method was developed for the more demanding case of preparing the europium porphyrin half-sandwich complex but applied later to both porphyrins and phthalocyanines. However, the reaction with a free base phthalocyanine affords the bis(phthalocyanine) double decker rather than the half-sandwich complex.

III. Synthesis of Double Deckers and Triple Deckers using $EuCl[N(SiMe_3)_2]_2$. The synthesis of triple deckers was the main focus of this work. However, to probe the reactivity of the (Por)EuX half-sandwich complex, we first investigated the synthesis of double deckers using this reagent.

(Por)Eu(Pc) Double Deckers. The porphyrin was added to a 4-fold excess of $EuCl[N(SiMe_3)_2]_2$ prepared in situ in bis(2-methoxyethyl) ether, and the resulting mixture was refluxed for ca. 3 h.[32] The metalation of the porphyrin leads to a characteristic change in the pattern of the Q-bands in the absorption spectrum.[14] The metalated porphyrin was stable in dilute solution, as determined by UV−vis spectroscopy. The europium porphyrin half-sandwich complex was then treated with a dilithium phthalocyanine to obtain sandwich complexes. The best results were obtained by using a 2-fold excess of a dilithium

Scheme 3



R^1 = *p*-tolyl, R^2/R^3 = H: (TTP)Eu(^{u}Pc)
R^1 = *p*-tolyl, R^2/R^3 = H/(*t*-Bu): (TTP)Eu(tBPc)

R^2/R^3 = H: (^{u}Pc)Eu(^{u}Pc)
R^2/R^3 = H/(*t*-Bu): (tBPc)Eu(tBPc)

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[27] Aspinall, H. C.; Bradley, D. C.; Hursthouse, M. B.; Sales, K. D.; Walker, N. P. C.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1989**, 623−626.

[28] Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021−1023.

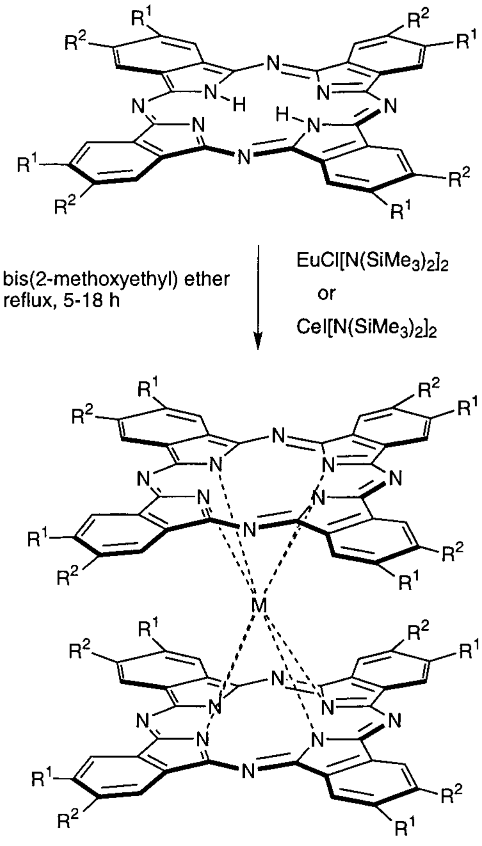
[29] Wong, W.-K.; Zhang, L.; Wong, W.-T.; Xue, F.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1999**, 615−622.

[30] Use of 3 molar equiv of $LiN(SiMe_3)_2$ for reaction with $LnCl_3$, which affords $Eu[N(SiMe_3)_2]_3$,[27] in our hands did not afford stable solutions of the europium porphyrin half-sandwich complex. In contrast, $Ln[N(SiMe_3)_2]_3$ afforded Ln(Por) half-sandwich complexes with Ln = Y, Yb.[29]

[31] Our provisional assignment for the (Por)EuX half-sandwich has X = Cl, but the structure with X = $N(SiMe_3)_2$ cannot be ruled out on the basis of the data at hand. However, three arguments in favor of X = Cl are as follows. (1) The reaction with a free base porphyrin in the formation of a half-sandwich complex is expected to lead to amine elimination (2 $HN(SiMe_3)_2$) rather than HCl + $HN(SiMe_3)_2$; moreover the presence of the weak acid $HCl{\cdot}HN(SiMe_3)_2$ would be expected to displace a $(Por)Eu[N(SiMe_3)_2]$ complex. (2) The subsequent reaction of (Por)EuX with a $PcLi_2$ is expected to give elimination of inorganic salt (LiCl) rather than the lithium amide ($LiN(SiMe_3)_2$). (3) The structure where X = $N(SiMe_3)_2$ is inconsistent with other data in which the porphyrin half-sandwich complex derived from $Eu[N(SiMe_3)_2]_3$ was not stable and underwent slow demetalation. The same reasoning holds for the provisional assignment of X′ = I in the structure of (Por)CeX′, but X′ = $N(SiMe_3)_2$ also cannot be ruled out.

[32] Bis(2-methoxyethyl) ether has bp 162 °C; the oil bath temperature for these reactions was set at ∼170 °C.

Scheme 4



(Pc)M(Pc)

M = Eu
$R^1 = R^2 = H$: 71%
$R^1/R^2 = H/(t\text{-Bu})$: 77%
$R^1 = R^2$ = heptyl: 83%
$R^1 = R^2$ = octyloxy: 89%

M = Ce
$R^1/R^2 = H/(t\text{-Bu})$: 74%
$R^1 = R^2$ = octyloxy: 66%

phthalocyanine, because the latter reacts with the porphyrin half-sandwich as well as with the excess $EuCl[N(SiMe_3)_2]_2$ remaining from the porphyrin metalation process. The main products in these reactions were the double-decker complexes (Por)Eu(Pc) and (Pc)Eu(Pc) (Scheme 3). The separation was performed by repeated column chromatography, typically two silica columns ($CHCl_3$) followed by one size-exclusion chromatography (SEC) column (THF). During the course of the first column chromatography procedure, the reduced $(Por)Eu(Pc)^-$ (green) and $(Pc)_2Eu^-$ (blue) double-decker species were oxidized to the corresponding neutral forms (brown for (Por)Eu(Pc); green for $(Pc)_2Eu$). This type of behavior has been described by Jiang et al.[33] To overcome the low solubility of the ^{u}Pc-containing complexes, prior to the chromatographic workup, the crude reaction mixture was stirred overnight with silica gel in $CHCl_3$ to oxidize the reduced species of the double deckers, yielding the neutral forms. In so doing, better separation in the chromatographic step (silica, $CHCl_3$) was obtained.

Thus, treatment of the $EuCl[N(SiMe_3)_2]_2$ solution with $TTPH_2$ gave the metalated porphyrin. The subsequent reaction with unsubstituted phthalocyanine $^{u}PcH_2$ afforded the (TTP)Eu(^{u}Pc) double decker in 38% yield. The use of dilithium tetra-*tert*-butylphthalocyanine in the same reaction gave the more soluble double decker (TTP)Eu(tBPc) in 94% yield (Scheme 3).

(Pc)Eu(Pc) Double Deckers. For the preparation of phthalocyanine sandwich complexes, we performed studies of the reaction of a free base phthalocyanine with the $EuCl[N(SiMe_3)_2]_2$ reagent prepared in situ. In general, the reaction of $EuCl[N(SiMe_3)_2]_2$ and a free base phthalocyanine in refluxing bis(2-methoxyethyl) ether for 5−18 h gave the corresponding (Pc)Eu(Pc) double decker. Thus, the reaction of $^{u}PcH_2$, $tBPcH_2$, $tBNcH_2$, $(heptyl)_8PcH_2$, or $(octyloxy)_8PcH_2$ gave $(^{u}Pc)_2Eu$, $(tBPc)_2Eu$, $(tBNc)_2Eu$, $[(heptyl)_8Pc]_2Eu$, or $[(octyloxy)_8Pc]_2Eu$ in yields >61% (Scheme 4).[34] These results show the higher reactivity of the phthalocyanines compared to the porphyrins. The only byproducts observed in these reactions were the free base phthalocyanine starting material and, in the case of tetra-*tert*-butylphthalocyanine, traces of the homoleptic triple decker (tBPc)Eu(tBPc)Eu(tBPc), as observed by preparative SEC and analysis by LD-MS. Separation was achieved by one silica column ($CHCl_3$) and one SEC (THF) column (except for the reaction with $^{u}PcH_2$, due to solubility problems).

It is noteworthy that a variety of methods have been developed for the synthesis of lanthanide double deckers, including directed routes and statistical routes.[35−50] The route

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(33) Jiang, J.; Choi, M. T. M.; Law, W.-F.; Chen, J.; Ng, D. K. P. *Polyhedron* **1998**, *17*, 3903−3908.

(34) A trial to make the double decker of 1,4,8,11,15,18,22,25-octabutoxyphthalocyanine led to the decomposition of the starting material.

(35) *Homoleptic phthalocyanine double deckers* have been prepared by cyclotetramerization of a phthalonitrile in the presence of a $Ln(OAc)_3$ alone[36] or under Shiraishi conditions[37] in the presence of DBU in a long-chain alcohol at reflux.[38−41] *Homoleptic porphyrin double deckers* have been prepared by reaction of a free base porphyrin with $Ln(acac)_3$ in refluxing 1,2,4-trichlorobenzene[42] or by reaction of a (porphyrin)M(acac) half-sandwich complex with a porphyrin−dilithium species.[43] *Heteroleptic porphyrin double deckers* have been prepared via a statistical reaction of two free base porphyrins with $Ln(acac)_3$ in refluxing 1,2,4-trichlorobenzene.[44] *Heteroleptic phthalocyanine double deckers* have been prepared via statistical reaction of two dilithium phthalocyanines in the presence of $Ln(acac)_3$ in refluxing chloronaphthalene.[24,45] A directed approach employed reaction of $PcLi_2$ with $Ln(acac)_3$ to form the (Pc)M(acac) half-sandwich complex, which provides a template to direct the cyclotetramerization of a phthalonitrile under Shiraishi conditions[37] to form the second phthalocyanine.[46] *Porphyrin−phthalocyanine double deckers* have been prepared via a number of routes: (a) directed reaction of $PcLi_2$ with $Ln(acac)_3$ at 120 °C to form the half-sandwich complex, followed by reaction with a free base porphyrin in refluxing 1,2,4-trichlorobenzene,[47] (b) directed reaction of (Pc)M(acac) with a free base porphyrin, or (Por)M(acac) with $PcLi_2$, in refluxing 1,2,4-trichlorobenzene,[48] (c) directed reaction under Shiraishi conditions[37] using (Por)M(acac) as a template to direct the cyclotetramerization of a phthalonitrile,[33,49] and (d) a one-flask reaction under Shiraishi conditions[37] of a free base porphyrin, $Ln(acac)_3$, and a naphthalonitrile.[50]

(36) Kirin, I. S.; Moskalev, P. N.; Makashev, Y. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1965**, *10*, 1065−1066.

(37) (a) Tomoda, H.; Saito, S.; Ogawa, S.; Shiraishi, S. *Chem. Lett.* **1980**, 1277−1280. (b) Tomoda, H.; Saito, S.; Shiraishi, S. *Chem. Lett.* **1983**, 313−316.

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(41) Nyokong, T.; Furuya, F.; Kobayashi, N.; Du, D.; Liu, W.; Jiang, J. *Inorg. Chem.* **2000**, *39*, 128−135.

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(46) Jiang, J.; Liu, W.; Law, W.-F.; Lin, J.; Ng, D. K. P. *Inorg. Chim. Acta* **1998**, *268*, 141−144.

described herein is a directed route. In some respects, the directed route we have employed resembles Linstead's method in the original discovery of double deckers, in which (Pc)SnCl$_2$ was reacted with PcLi$_2$, affording the corresponding (Pc)Sn(Pc).[51] A directed route is superior to statistical procedures for the preparation of heteroleptic porphyrin double deckers or heteroleptic phthalocyanine double deckers. A directed route is not needed to prepare homoleptic phthalocyanine double deckers or homoleptic porphyrin double deckers.

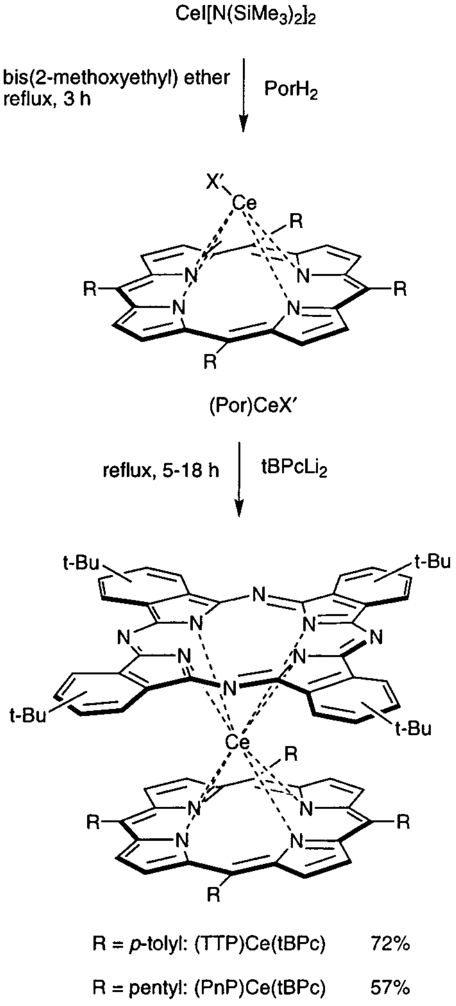
Triple Deckers. To prepare triple deckers, the porphyrin half-sandwich (Por)EuX was reacted with several different double-decker compounds. The double deckers were used in the neutral or reduced forms. The reduced form of the (Por)Eu(Pc) double decker (Por = TTP; Pc = ^{u}Pc, tBPc) was generated in bis(2-methoxyethyl) ether by reaction with an equimolar amount of NaBH$_4$ in bis(2-methoxyethyl) ether at room temperature for 24 h. In the course of this reaction the mixture underwent a characteristic change in color from brown to green. The reduced form of the (Pc)$_2$Eu double decker (Pc = ^{u}Pc, tBPc) was obtained similarly, affording a color change from green to blue during the course of reduction. All double-decker species containing the unsubstituted phthalocyanine were poorly soluble in bis(2-methoxyethyl) ether.

Thus, the reaction of (TTP)EuX (3 or 1.5 molar equiv) with either the neutral or reduced form of the double decker (tBPc)$_2$Eu in refluxing bis(2-methoxyethyl) ether for 20 h afforded the triple decker in 16% or 17% yield, respectively.[52] In comparison with the good yields obtained in the reactions of the (Por)Eu(acac) half-sandwich complex with the (tBPc)$_2$Eu double decker (vide supra) in refluxing 1,2,4-trichlorobenzene via the Weiss method, these results showed that triple deckers of the type (Por)Eu(tBPc)Eu(tBPc) could be obtained using a (Por)EuX half-sandwich complex, but with no improvement in yield.

Triple deckers of the type (Por^1)M(Pc)M(Por^2) are attractive but have not been employed for information-storage applications due to lack of suitable synthetic methods. We investigated the synthesis of these types of triple deckers by the reaction of the (TPP)EuX half-sandwich complex with the double-decker species (Por)Eu(Pc) (Por = TTP; Pc = ^{u}Pc, tBPc). The reaction using the double decker (TTP)Eu(^{u}Pc) met with failure. After reaction of (TPP)EuX with (TTP)Eu(tBPc) for 24 h in refluxing bis(2-methoxyethyl) ether, the LD-MS spectrum of the reaction mixture showed a peak indicating that the expected triple decker (TPP)Eu(tBPc)Eu(TTP) was a minor product. However, the isolated yield was quite low, and insufficient material was obtained for full characterization. A longer reaction time afforded no increase in yield. The reduced form of the double decker afforded a similar reaction pattern.

In summary, the reaction of the (Por)EuX half-sandwich complex with (tBPc)Eu(tBPc) but not (^{u}Pc)Eu(^{u}Pc) affords the corresponding triple decker. The reaction is performed at lower temperature (~170 °C) than the Weiss method (~230 °C), affording the triple decker devoid of scrambling, albeit in low yield. While the restriction to the use of the tBPc ligand may seem quite limiting, triple deckers composed of ligands bearing electron-releasing substituents are highly attractive for information storage applications.[7] In addition, the presence of the *tert*-butyl substituents affords increased solubility. Thus, we decided to continue examining the scope of this method using the tBPc macrocycle and CeI$_3$ as a starting material.[53] Cerium-containing triple deckers are attractive for molecular information storage applications, given their additional cationic oxidation states compared with those of other lanthanide triple deckers.

Scheme 5



IV. Synthesis of Double Deckers and Triple Deckers using CeI[N(SiMe$_3$)$_2$]$_2$. The procedure for the in situ preparation of EuCl[N(SiMe$_3$)$_2$]$_2$ was applied to CeI$_3$ with minor changes. (1) CeI$_3$ was treated with 2 molar equiv of LiN(SiMe$_3$)$_2$ (THF solution) in bis(2-methoxyethyl) ether at 0 °C. (2) The mixture was warmed to room temperature (1 h) and then was refluxed for 1 h to obtain complete reaction of the CeI$_3$ (CeI$_3$ in the form of beads reacts to completion only under vigorous conditions). The resulting solution of CeI[N(SiMe$_3$)$_2$]$_2$ was used in reactions with porphyrins (Ce:porphyrin ratio >4:1) to obtain the corresponding porphyrin half-sandwich complexes, which are formulated as (Por)CeX′ where X′ = I, N(SiMe$_3$)$_2$ by

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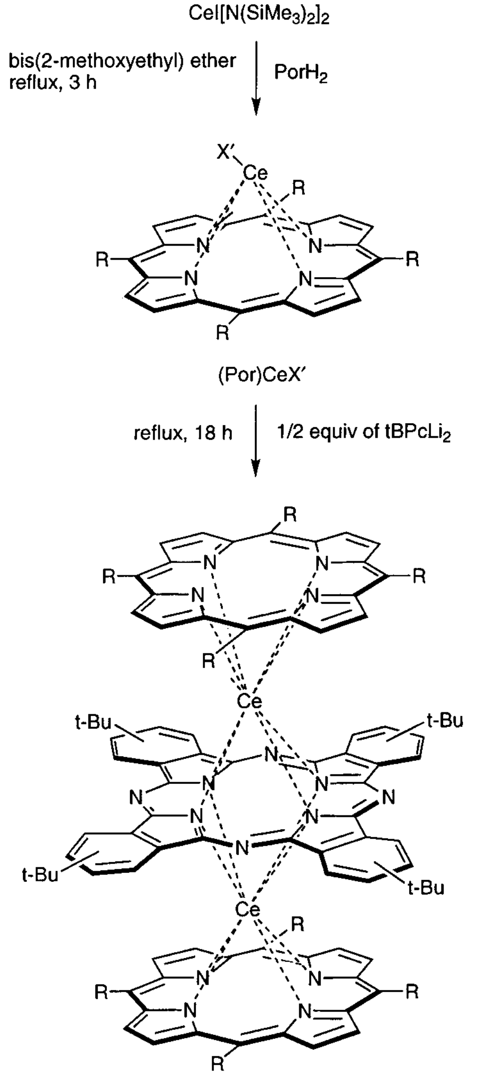
(52) The reaction of (Por)EuX and a double-decker species was performed for 20 h at reflux in bis(2-methoxyethyl) ether. The product was isolated by chromatography (one silica column, one SEC column). Yields are based on the amount of the bis(phthalocyanine) species.

(53) We also tried to use LuI$_3$ under the same conditions employed with CeI$_3$. However, no metalation of the porphyrin was observed by UV–vis spectroscopy.

Scheme 6



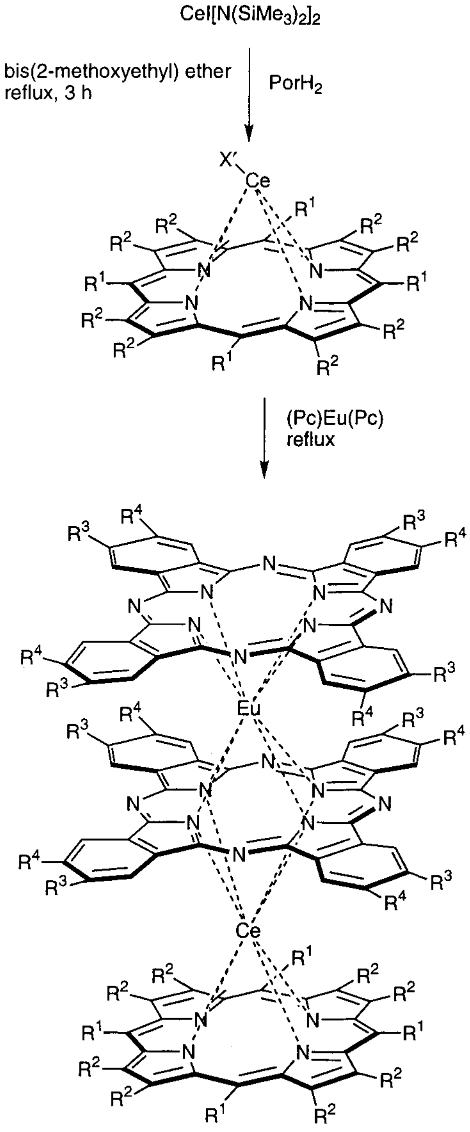
R = *p*-tolyl: (TTP)Ce(tBPc)Ce(TTP) 13%
+
byproduct = (TTP)Ce(tBPc) 41%

R = pentyl: (PnP)Ce(tBPc)Ce(PnP) 13%
+
byproduct = (PnP)Ce(tBPc) 45%

analogy with the (Por)EuX complexes.[31] The completeness of metalation was again estimated by UV−vis spectroscopy. It is noteworthy that the (Por)CeX′ complexes formed stable solutions, similar to the case of the (Por)EuX half-sandwich complex. In contrast, (Por)Ce(acac) complexes have been reported to be unstable.[14] In the following, we examine the synthesis of double deckers as a prelude to the synthesis of triple deckers.

(Por)Ce(tBPc) Double Deckers. The reaction of $TTPH_2$ with the $CeI[N(SiMe_3)_2]_2$ reagent (generated in solution) followed by treatment with an equimolar amount of $tBPcLi_2$ gave the green double decker (TTP)Ce(tBPc) in 72% yield. The use of $PnPH_2$ in the same reaction led to (PnP)Ce(tBPc) in 57% yield (Scheme 5). Thus, the reaction of the (Por)CeX′ half-sandwich complex with an equimolar amount of $tBPcLi_2$ cleanly gave the double-decker species (Por)Ce(tBPc). In contrast to the reaction with the europium analogue, in these reactions no bis(phthalocyanine) double decker (i.e., $(tBPc)_2Ce$) was observed.

Scheme 7



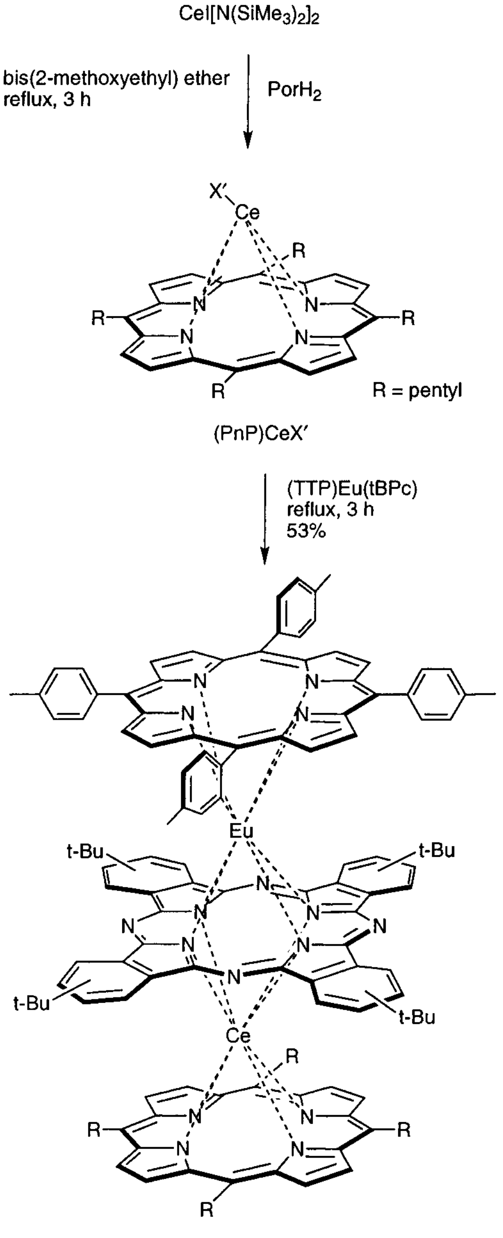
R^1	R^2	R^3	R^4	Yield
p-tolyl	H	H	*t*-Bu	53%
p-tolyl	H	octyloxy	octyloxy	39%
H	ethyl	H	*t*-Bu	38%

The different color (green) of (Por)Ce(Pc) complexes compared with that of the europium double deckers (Por)Eu(Pc) (brown) is attributed to the different redox states of the metals and ligands: the europium complex is formulated as the radical species $(Por^{2-})Eu^{3+}(Pc^{\bullet-})$ and the cerium complex as the closed-shell species $(Por^{2-})Ce^{4+}(Pc^{2-})$.

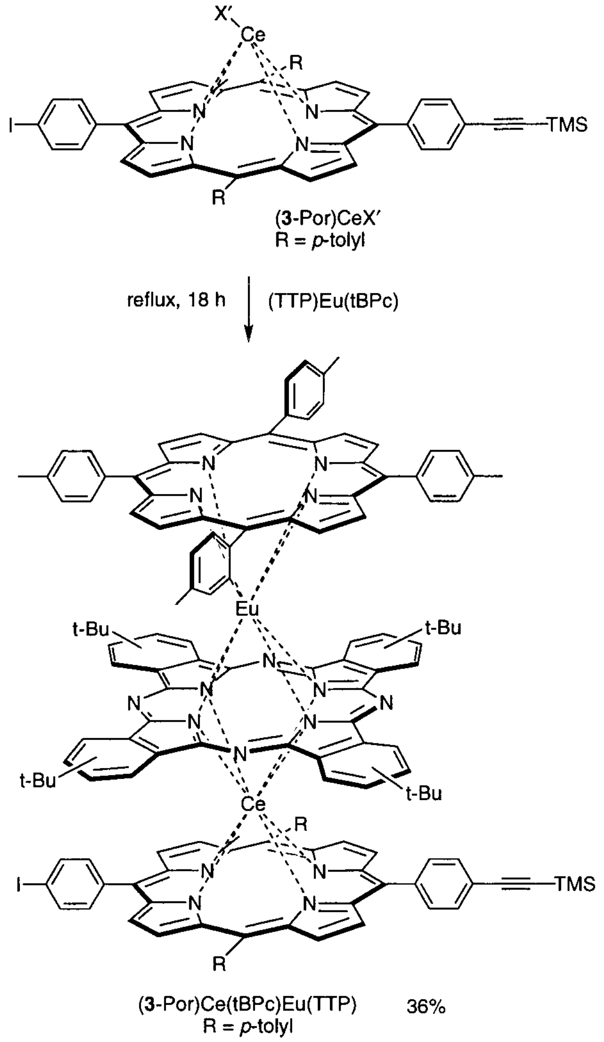
(Pc)Ce(Pc) Double Deckers. The reaction of $tBPcH_2$ with the $CeI[N(SiMe_3)_2]_2$ reagent (generated in solution) gave the green double decker (tBPc)Ce(tBPc) in 74% yield. The use of $(octyloxy)_8PcH_2$ in the same reaction led to $[(octyloxy)_8Pc]Ce[(octyloxy)_8Pc]$ in 66% yield (Scheme 4). Thus, the reaction of PcH_2 with an excess of $CeI[N(SiMe_3)_2]_2$ complex cleanly gave the double-decker species (Pc)Ce(Pc).[34]

Triple Deckers. The absence of the (tBPc)Ce(tBPc) double decker in the reactions to make the heteroleptic (Por)Ce(tBPc) double deckers suggested that $tBPcLi_2$ exhibits a preference for reaction with the cerium porphyrin half-sandwich complex vs

Scheme 8



Scheme 9



the $CeI[N(SiMe_3)_2]_2$. Thus, we examined reactions of the (Por)CeX′ half-sandwich complex with only 0.5 equiv of $tBPcLi_2$ (relative to the porphyrin). Considering the greater reactivity of this half-sandwich complex and no side reaction of $tBPcLi_2$ with the excess $CeI[N(SiMe_3)_2]_2$, a triple decker of the type (Por)Ce(tBPc)Ce(Por) should be produced. This expectation was confirmed by using *meso*-tetra-*p*-tolylporphyrin or *meso*-tetrapentylporphyrin in reactions with $CeI[N(SiMe_3)_2]_2$ followed by treatment with 0.5 equiv of $tBPcLi_2$; the triple deckers (TTP)Ce(tBPc)Ce(TTP) and (PnP)Ce(tBPc)Ce(PnP) were each obtained in 13% yield. The double-decker complex (TTP)Ce(tBPc) or (PnP)Ce(tBPc) was isolated as a byproduct in 41% or 45% yield, respectively (Scheme 6). However, an attempt to prepare the (TTP)Ce(Nc)Ce(TTP) triple decker by this method met with recovery of the starting materials, probably because of the poor solubility of the $NcLi_2$ in the reaction mixture.

The success in preparing triple deckers of the type (Por)Ce(tBPc)Ce(Por) prompted us to explore reactions of the (Por)CeX′ half-sandwich complex with double deckers. Given that the neutral or reduced form of $(tBPc)_2Eu$ gave the (Por)Eu(tBPc)Eu(tBPc) triple decker in nearly identical yield upon reaction with the (Por)EuX half-sandwich complex, in subsequent studies we used the neutral form of each double-decker complex, which is the species normally obtained upon purification.

Our first studies focused on the use of (Por)Ce(Pc) double deckers. The reaction of the (PnP)CeX′ half-sandwich complex with (TTP)Ce(tBPc) gave a mixture comprised predominantly of three triple deckers of type (Por)Ce(tBPc)Ce(Por) in almost statistical ratio as estimated by LD-MS. This intractable mixture of $(Por^1)Ce(tBPc)Ce(Por^1)$, $(Por^1)Ce(tBPc)Ce(Por^2)$, and $(Por^2)Ce(tBPc)Ce(Por^2)$ likely stems from cleavage of the double decker prior to the formation of the triple decker. Similarly, the reactions of the (TTP)CeX′ half-sandwich with the phthalocyanine double deckers (tBPc)Ce(tBPc) and $[(octyloxy)_8Pc]_2Ce$ mostly afforded the (TTP)Ce(Pc) type double deckers along with the starting double decker and a tiny amount of the expected triple decker, also suggesting cleavage of the starting double decker.

Given that both the heteroleptic and the homoleptic double deckers of cerium are unstable under these reaction conditions, by using a europium double decker in the reaction with the (Por)CeX′ half-sandwich we hoped to avoid such scrambling processes. Thus, the reaction of (TTP)CeX′ with the double decker $(tBPc)_2Eu$ or $[(octyloxy)_8Pc]_2Eu$ in refluxing bis(2-methoxyethyl) ether for 18−24 h gave the expected triple decker (TTP)Ce(tBPc)Eu(tBPc) or (TTP)Ce[(octyloxy)$_8$Pc]Eu-[(octyloxy)$_8$Pc] in 53% or 39% yield.[54] Similarly, the reaction of (OEP)CeX′ with the (tBPc)$_2$Eu double decker in refluxing bis(2-methoxyethyl)ether for 18 h gave the expected triple decker (OEP)Ce(tBPc)Eu(tBPc) in 38% yield (Scheme 7).

The synthesis of triple deckers of the type (Por^1)Eu(tBPc)-Ce(Por^2) was examined. The reaction of (PnP)CeX′ and (TTP)Eu(tBPc) for 3 h in refluxing bis(2-methoxyethyl) ether gave the expected triple decker (PnP)Ce(tBPc)Eu(TTP) in 53% yield (Scheme 8). No other triple deckers were obtained. This approach was applied to the synthesis of a triple decker bearing two functional handles. Thus, the reaction of CeI[N(SiMe$_3$)$_2$]$_2$ with a monoiodo monoethynyl porphyrin (**3**-PorH$_2$)[55] afforded the corresponding cerium porphyrin half-sandwich complex. Reaction of the latter with (TTP)Eu(tBPc) in refluxing bis(2-methoxyethyl) ether for 18 h afforded the triple decker (**3**-Por)-Ce(tBPc)Eu(TTP) in 36% yield (Scheme 9). Traces of other triple deckers were observed by LD-MS; these species were removed by SEC. This particular triple decker, (**3**-Por)Ce(tBPc)-Eu(TTP), is a useful building block for elaboration into arrays.

In summary, the reaction of the (Por)CeX′ half-sandwich complex and either a (tBPc)$_2$Eu double decker or a (Por)Eu-(tBPc) double decker afforded the expected triple decker in good yield, generally with little or no observable scrambling. This approach affords facile access to triple deckers of the type (tBPc)Eu(tBPc)Ce(Por) or (Por^1)Eu(tBPc)Ce(Por^2).

Conclusions

The use of lanthanide porphyrin phthalocyanine triple-decker sandwich molecules for molecular information storage applications requires synthetic methodology that enables (1) the selective preparation of a given type of triple decker, (2) the incorporation of substituents at desired locations on the ligands in the triple deckers, and (3) incorporation of two lanthanides of choice in the triple decker. The common “reaction-of-monomers” synthesis of lanthanide triple deckers affords a mixture of double deckers and triple deckers comprised of one metal and does not enable the introduction of different substituents in the two porphyrin or two phthalocyanine ligands in the triple decker. This method constrained our initial studies in molecular information storage to the use of triple deckers of type (Pc)Eu(Pc)Eu(Por). The directed “monomer + dimer” synthesis of Weiss (demonstrated with M = Gd, Lu, Y, La, Ce) employs the reaction of a (Por^1)M^1(acac) half-sandwich complex with a (Pc)M^2(Por^2) double-decker complex in refluxing 1,2,4-trichlorobenzene (bp 214 °C). Greater selectivity is obtained, as the main product is (Por^1)M^1(Pc)M^2(Por^2) in the cases reported. We applied this method as described herein to obtain several (Pc)Eu(Pc)Eu(Por) triple deckers with good results, but attempts to prepare the (Por^1)Eu(Pc)Eu(Por^2) triple decker gave a mixture of triple deckers.

We have developed a somewhat milder method that employs the lanthanide reagent EuCl[N(SiME$_3$)$_2$]$_2$ or CeI[N(SiME$_3$)$_2$]$_2$, generated in situ, which is reacted with a porphyrin in refluxing bis(2-methoxyethyl) ether (bp 162 °C) to give the porphyrin half-sandwich complex provisionally formulated as (Por)EuCl or (Por)CeI.[31] The reaction of (Por)EuX with a dilithium phthalocyanine gave the double-decker complexes (Por)Eu(Pc) and (Pc)Eu(Pc). Similar reaction with (tBPc)Eu(tBPc) gave the corresponding triple decker (tBPc)Eu(tBPc)Eu(Por). The reaction of (Por)CeX′ with 1 molar equiv of tBPcLi$_2$ gave the (Por)Ce(tBPc) double decker; the reaction with 0.5 molar equiv of tBPcLi$_2$ gave the (Por)Ce(tBPc)Ce(Por) triple decker accompanied by the (Por)Ce(tBPc) double decker. Similar reactions of (Por)CeX′ with europium double deckers (Por^2)Eu(tBPc) and (tBPc)$_2$Eu were employed to prepare the triple deckers (Por^1)Ce(tBPc)Eu(Por^2) and (Por^1)Ce(tBPc)Eu(tBPc). The rational synthesis of heteroleptic heteronuclear triple-decker complexes by reaction of a porphyrinic half-sandwich complex with a double-decker compound allows the specific introduction of a functionalized porphyrin into the triple decker, enabling further incorporation into triple-decker arrays. The ability to prepare triple deckers of type (Por^1)Ce(tBPc)Eu(Por^2) is especially attractive, because one porphyrin can be derivatized with synthetic handles (e.g., thiol linkers or groups for preparing arrays) while the second porphyrin carries substituents chosen to alter the electrochemical potential of the complex. The application of this method to prepare triple-decker monomers for incorporation into arrays for multibit information storage is presently under investigation.

Experimental Section

General Considerations. ^{1}H NMR spectra were collected in CDCl$_3$ (300 MHz) unless noted otherwise. Absorption spectra (HP 8451A, Cary 3) were collected in toluene. Porphyrin−phthalocyanine sandwich complexes were analyzed by laser desorption mass spectrometry (LD-MS; Bruker Proflex II) and a high-resolution fast atom bombardment mass spectrometer (FAB-MS; JEOL HX 110HF). LD-MS analysis was done without a matrix[56] or with the matrix 1,2-bis(5-phenyloxazol-2-yl)benzene (POPOP). High-resolution mass spectrometry was carried out at greater than unit resolution. ^{1}H NMR spectroscopy proved uninformative for (1) all double deckers that incorporate europium and (2) all double deckers and triple deckers comprised of tetra-*tert*-butyl-substituted phthalocyanines. The double deckers were generally characterized by TLC, UV−vis, LD-MS, and FAB-MS. The triple deckers were characterized by TLC, UV−vis, ^{1}H NMR, LD-MS, and FAB-MS. We emphasize again that each europium double decker isolated is assumed to be a radical species unless noted otherwise but this is not designated in the nomenclature (e.g., (Por)Eu(Pc)) employed.

All operations involving organometallic compounds were carried out under argon using standard Schlenk techniques. Eu(acac)$_3$·nH$_2$O was obtained from Alfa Aesar. Bis(2-methoxyethyl) ether was used as received from Aldrich (anhydrous, water <0.005%). Unless otherwise indicated, all other reagents were obtained from Aldrich Chemical Co. and all solvents were obtained from Fisher Scientific. The following phthalocyanines were obtained commercially: tetra-*tert*-butylphthalocyanine (tBPcH$_2$, mixture of regioisomers), naphthalocyanine (NcH$_2$), tetra-*tert*-butylnaphthalocyanine (tBNcH$_2$, mixture of regioisomers), 2,3,9,10,16,17,23,24-octakis(octyloxy)phthalocyanine ((octyloxy)$_8$PcH$_2$) and dilithium phthalocyanine (^{u}PcLi$_2$, dye content ∼70%) were obtained from Aldrich; phthalocyanine (^{u}PcH$_2$) was obtained from Kodak; octaethylporphyrin (OEPH$_2$) was obtained from Midcentury Chemicals. 2,3,9,10,16,17,23,24-Octaheptylphthalocyanine[57] ((heptyl)$_8$PcH$_2$) was obtained as a byproduct of statistical reactions yielding mixtures of phthalocyanines.[58] The dilithium derivative tBPcLi$_2$ was prepared from 4-*tert*-butylphthalonitrile;[24] the other dilithium phthalocyanines ((octyloxy)$_8$PcLi$_2$, (heptyl)$_8$PcLi$_2$, NcLi$_2$) were prepared by lithiation of the free base species.[7] Synthetic porphyrins were prepared via the Adler

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[54] In the case of the [(octyloxy)$_8$Pc]$_2$Eu double-decker reaction, TTPH$_2$ was used in excess because use of a stoichiometric ratio of the starting materials resulted in difficulty of separating the triple decker and starting double decker. Accordingly, the yield has been calculated from the amount of double decker used.

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method[59] (*meso*-tetra-*p*-tolylporphyrin, *meso*-tetraphenylporphyrin), the two-step one-flask synthesis (*meso*-tetrapentylporphyrin),[60] or new rational synthetic methods (5,15-bis(4-iodophenyl)-10,20-di-*p*-tolylporphyrin (**1**-PorH_2),[22] 5-[4-[2-(trimethylsilyl)ethynyl]phenyl]-15-[4-[2-(triisopropylsilyl)ethynyl]phenyl]-10,20-di-*p*-tolylporphyrin (**2**-PorH_2),[22] 5-(4-iodophenyl)-15-[4-[2-(trimethylsilyl)ethynyl]phenyl]-10,20-di-*p*-tolylporphyrin (**3**-PorH_2[55]).

Calculated yields for porphyrin-containing sandwich molecules are generally based on the amount of porphyrin employed. The yields for (Pc)Eu(Pc) double deckers are based on the phthalocyanine. The number of moles of a PcLi_2 compound is taken to be 70% for a given mass of ^{u}PcLi_2, 97% for tBNcLi_2, and 100% for other PcLi_2 species. For $Eu(acac)_3 \cdot nH_2O$, the value of *n* is assumed to be 2.5 for calculating the quantity of material in the reactions.

Chromatography. Adsorption column chromatography was performed using flash silica (Baker, 60−200 mesh). Preparative-scale size exclusion chromatography (SEC) was performed using BioRad Biobeads SX-1. A preparative-scale glass column (4.8 × 60 cm) was packed using Biobeads SX-1 in THF and eluted with gravity flow. Analytical scale SEC was performed with a Hewlett-Packard 1090 HPLC using a 1000 Å column (5 μL, styrene−divinylbenzene copolymer) with THF as eluent (0.8 mL/min).[61]

1. Europium Double Deckers: Exemplary Procedure for the in Situ Preparation of $EuCl[N(SiMe_3)_2]_2$, Given for the Synthesis of (TTP)Eu(^{u}Pc). To a vigorously stirred suspension of $EuCl_3$ (100.7 mg, 0.390 mmol) in bis(2-methoxyethyl) ether (5 mL) at 0 °C was slowly added a solution of $LiN(SiMe_3)_2$ (780 μL, 0.780 mmol, 1 M in THF). Stirring was continued while the mixture was warmed to room temperature (ca. 1 h). The mixture was stirred at room temperature for 1 h. (This constitutes the standard procedure for preparing $EuCl[N(SiMe_3)_2]_2$ in situ.) A sample of *meso*-tetra-*p*-tolylporphyrin (45.3 mg, 67.5 μmol) was added. The mixture was refluxed in an oil bath at ∼170 °C for ca. 3 h while the progress of the reaction was monitored by UV−vis spectroscopy. After metalation of the porphyrin was complete, ^{u}PcLi_2 (102 mg, 135 μmol) was added and the mixture was further refluxed for 18 h. The mixture was cooled and concentrated, and $CHCl_3$ (100 mL) and silica gel (15 g) were added. This mixture was stirred overnight, which led to a color change from green to brown-green. The mixture was concentrated and chromatographed (silica, $CHCl_3$), affording three bands (first band purple, second band brown, third band green). The first band was not collected. The third band was again chromatographed and finally washed with hexanes to give (^{u}Pc)Eu(^{u}Pc)[38] as a green solid (49 mg, 62%). The second band was further chromatographed (silica, toluene) to give the title compound as a brown solid (34.0 mg, 38%). LD-MS (*m*/*z*): obsd 1333.39. FAB-MS (*m*/*z*): obsd 1333.7, calcd 1333.37 ($C_{80}H_{52}N_{12}Eu$). λ_{abs}: 324, 407, 476 nm.

(TTP)Eu(tBPc). The reaction of $EuCl[N(SiMe_3)_2]_2$, produced from $EuCl_3$ (60.2 mg, 0.233 mmol) and $LiN(SiMe_3)_2$ (466 μL, 0.466 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (5 mL) following the standard procedure, and *meso*-tetra-*p*-tolylporphyrin (39.0 mg, 58.1 μmol) gave after 3 h of reflux the solution of metalated porphyrin, as determined by UV−vis spectroscopy. A sample of tBPcLi_2 (84.5 mg, 0.115 mmol) was added, and the mixture was refluxed overnight (18 h). The mixture was cooled and concentrated. The residue was chromatographed (silica, $CHCl_3$), during which slow oxidation of the reduced form of the double deckers took place. Separation was obtained by repeating the same column to give two bands (first band brown, second band green). The first band (brown) was further purified by two SEC columns (THF) to give the title compound as a brown solid (85.4 mg, 94%). LD-MS (*m*/*z*): obsd 1557.6, 1542.51. FAB-MS (*m*/*z*): obsd 1557.62, calcd 1557.62 ($C_{96}H_{84}N_{12}Eu$). λ_{abs}: 330, 408, 476 nm. The second band (green) gave after SEC (THF) the green double decker (tBPc)Eu(tBPc) (9.6 mg, 10%).

(^{u}Pc)Eu(^{u}Pc). $EuCl[N(SiMe_3)_2]_2$ was produced in situ from $EuCl_3$ (111.9 mg, 0.433 mmol) and $LiN(SiMe_3)_2$ (866 μL, 0.866 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (5 mL) following the standard procedure. A sample of ^{u}PcH_2 (42.4 mg, 82.4 μmol) was added, and the mixture was refluxed for 6 h. The mixture was cooled and concentrated, and $CHCl_3$ (100 mL) and silica gel (15 g) were added. This mixture was stirred overnight, which led to a color change from blue to green. The mixture was concentrated and chromatographed (silica, $CHCl_3$). The only band (green) was collected, affording a green solid (34.2 mg, 71%). Analytical data were consistent with the literature.[38]

(tBPc)Eu(tBPc). $EuCl[N(SiMe_3)_2]_2$ was produced in situ from $EuCl_3$ (48.2 mg, 0.186 mmol) and $LiN(SiMe_3)_2$ (373 μL, 0.373 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (3 mL) following the standard procedure. A sample of tBPcH_2 (38.3 mg, 51.8 μmol) was added, and the mixture was refluxed for 4 h. The mixture was cooled, concentrated, and chromatographed (silica, $CHCl_3$). The first band (light blue, tBPcH_2) was not collected. The second band (green) was further purified by SEC (THF), affording a green solid (32.4 mg, 77%). Analytical data were consistent with the literature.[62]

(tBNc)Eu(tBNc). $EuCl[N(SiMe_3)_2]_2$ was produced in situ from $EuCl_3$ (106.5 mg, 0.412 mmol) and $LiN(SiMe_3)_2$ (825 μL, 0.825 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (6 mL) following the standard procedure. A sample of tBNcH_2 (103.4 mg, 107 μmol) was added, and the mixture was refluxed for 4 h. The mixture was cooled, concentrated, and chromatographed (silica, $CHCl_3$/methanol). The only band (blue) was collected, affording a blue solid (65.7 mg, 61%). Analytical data were consistent with the literature.[39]

[(octyloxy)$_8$Pc]$_2$Eu. $EuCl[N(SiMe_3)_2]_2$ was produced in situ from $EuCl_3$ (78.5 mg, 0.303 mmol) and $LiN(SiMe_3)_2$ (606 μL, 0.606 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (5 mL) following the standard procedure. A sample of (octyloxy)$_8$PcH_2 (76.9 mg, 49.9 μmol) was added, and the mixture was refluxed for 6 h. The mixture was cooled, concentrated, and chromatographed (silica, $CHCl_3$). The first band (green) was collected and further purified by SEC (THF), affording a green solid (71.7 mg, 89%). Analytical data were consistent with the literature.[63]

[(heptyl)$_8$Pc]$_2$Eu. $EuCl[N(SiMe_3)_2]_2$ was produced in situ from $EuCl_3$ (70.0 mg, 0.271 mmol) and $LiN(SiMe_3)_2$ (542 μL, 0.542 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (5 mL) following the standard procedure. A sample of (heptyl)$_8$PcH_2 (86.5 mg, 66.7 μmol) was added, and the mixture was refluxed for 4 h. The mixture was cooled, concentrated, and chromatographed (silica, $CHCl_3$). The first band (green) was collected and further purified by SEC (THF), affording a green solid (76.2 mg, 83%). Analytical data were consistent with the literature.[38]

2. Synthesis of a Triple Decker of Type (Por)Eu(Pc)Eu(Pc) via the Weiss Procedure, Given for (TTP)Eu(^{u}Pc)Eu(^{u}Pc). A mixture of *meso*-tetra-*p*-tolylporphyrin (12.5 mg, 18.6 μmol) and $Eu(acac)_3 \cdot nH_2O$ (32 mg, 0.065 mmol) in 1,2,4-trichlorobenzene (8 mL) was heated to reflux in an oil bath at ∼230 °C and stirred for 4 h. The resulting cherry red solution (containing the (TTP)Eu(acac) half-sandwich complex) was cooled to room temperature, and then the double decker (^{u}Pc)Eu(^{u}Pc) (22 mg, 0.019 mmol) was added. The mixture was refluxed for 18 h. Then the solvent was removed and the residue was chromatographed (silica, $CHCl_3$). The first band (purple, TTPH_2) was not collected. The second band (green) was collected and redissolved in $CHCl_3$/toluene for chromatography on silica (toluene). The first band afforded a green solid (8.8 mg, 24%). Analytical data were consistent with the literature.[6]

(OEP)Eu(tBPc)Eu(tBPc). A mixture of octaethylporphyrin (OEPH_2) (9.6 mg, 0.018 mmol) and $Eu(acac)_3 \cdot nH_2O$ (62.3 mg, 0.126 mmol) in 1,2,4-trichlorobenzene (5 mL) was heated to reflux and stirred for 3.5 h. The resulting cherry red solution was cooled to room temperature, the bis(phthalocyanine) europium double decker (tBPc)Eu(tBPc) (29.3 mg, 0.018 mmol) was added, and the mixture was refluxed for 18 h.

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The solvent was removed and the residue was chromatographed (silica, $CHCl_3$). The first band (purple, $OEPH_2$) was not collected. The second band (green, (tBPc)Eu(tBPc)) was not collected. The third band (blue) was collected and further purified by SEC (THF). The first band (blue) was collected, affording a blue solid (31.6 mg, 76%). A ^1H NMR spectrum was collected but the mixture of regioisomers made interpretation difficult. LD-MS (with POPOP) (*m*/*z*): obsd 2310.1, 1626.1, 673.0. FAB-MS (*m*/*z*): obsd 2310.69, 2311.0 calcd ($C_{132}H_{140}N_{20}Eu_2$). λ_{abs}: 342, 394, 623, 658, 724 nm.

(1-Por)Eu(tBPc)Eu(tBPc). A mixture of **1**-PorH_2 (40 mg, 0.045 mmol) and $Eu(acac)_3 \cdot nH_2O$ (140 mg, 0.284 mmol) in 1,2,4-trichlorobenzene (5 mL) was heated to reflux and stirred for 5 h. The resulting cherry red solution was cooled to room temperature, the bis(phthalocyanine) europium double decker (tBPc)Eu(tBPc) (72 mg, 0.044 mmol) was added, and the mixture was refluxed for 5 h. The solvent was removed, and the residue was chromatographed (silica, $CHCl_3$). The first band (purple, **1**-PorH_2) was not collected. The second band (green) was collected and further purified twice by SEC (THF). The first band (green-blue) was collected, affording a green-blue solid (82 mg, 69%). A ^1H NMR spectrum was collected, but the mixture of regioisomers made interpretation difficult. LD-MS (with POPOP) (*m*/*z*): obsd 2671.3, 2544.5, 1625.3. FAB-MS (*m*/*z*): obsd 2670.75, calcd 2670.69 ($C_{142}H_{126}N_{20}Eu_2$). λ_{abs}: 347, 418, 526, 621, 727 nm.

(2-Por)Eu(tBPc)Eu(tBPc). A mixture of **2**-PorH_2 (18 mg, 0.019 mmol) and $Eu(acac)_3 \cdot nH_2O$ (37 mg, 0.075 mmol) in 1,2,4-trichlorobenzene (4 mL) was heated to reflux and stirred for 4 h. The resulting cherry red solution was cooled to room temperature, the (tBPc)Eu(tBPc) double decker (28 mg, 0.017 mmol) was added, and the mixture was refluxed for 4 h. The solvent was removed, and the residue was chromatographed (silica, $CHCl_3$). The first band (purple, **2**-PorH_2) was not collected. The second band (green) was collected and further purified by SEC (THF). The first band (green-blue) was collected, affording a green-blue solid (38.5 mg, 75%). A ^1H NMR spectrum was collected, but the mixture of regioisomers made interpretation difficult. LD-MS (*m*/*z*): obsd 2693.3, 2678.2. FAB-MS (*m*/*z*): obsd 2695.10, calcd 2695.08 ($C_{158}H_{156}N_{20}Eu_2$). λ_{abs}: 347, 418, 527, 621, 729 nm.

3. Cerium Sandwich Complexes: Exemplary Procedure for the in Situ Preparation of CeI[N(SiMe$_3$)$_2$]$_2$, Given for the Synthesis of (TTP)Ce(tBPc). To a vigorously stirred suspension of CeI_3 (114 mg, 0.219 mmol) in bis(2-methoxyethyl) ether (5 mL) at 0 °C was slowly added a solution of $LiN(SiMe_3)_2$ (439 μL, 0.439 mmol, 1 M in THF). Stirring was continued while the mixture was warmed to room temperature (ca. 1 h). The solution was then refluxed in an oil bath at ~170 °C for 1 h, during which the cerium beads reacted and a fine precipitate (presumably LiI) was obtained. This constitutes the standard procedure for preparing $CeI[N(SiMe_3)_2]_2$ in situ. Then *meso*-tetra-*p*-tolylporphyrin (35.1 mg, 52.3 μmol) was added and the mixture was refluxed for ca. 3 h while the progress of the reaction was monitored by UV−vis spectroscopy. After formation of the porphyrin half-sandwich complex was complete, tBPcLi$_2$ (42.5 mg, 56.7 μmol) was added and the mixture was further refluxed for 5 h. The mixture was cooled and concentrated. The residue was chromatographed (silica, $CHCl_3$, then $CHCl_3$/methanol (10:1)). No separation was observed, perhaps due to slow decomposition of iodine complexes of the sandwich molecules. Therefore, only one fraction was collected, which was further separated by SEC (THF). The first band (green) was chromatographed again by SEC. A final chromatography (silica, $CHCl_3$) afforded a green solid (57.9 mg, 72%). LD-MS (*m*/*z*): obsd 1544.4, 1530.8, 807.54. FAB-MS (*m*/*z*): obsd 1544.60, calcd 1544.60 ($C_{96}H_{84}N_{12}Ce$). λ_{abs}: 338, 403, 470, 628 nm.

(PnP)Ce(tBPc). A solution of $CeI[N(SiMe_3)_2]_2$, prepared in situ by reaction of CeI_3 (229 mg, 0.441 mmol) and $LiN(SiMe_3)_2$ (882 μL, 0.882 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (8 mL) following the standard procedure, was reacted with *meso*-tetrapentylporphyrin (57.3 mg, 97.0 μmol) at reflux for 3 h, affording the metalated porphyrin as determined by UV−vis spectroscopy. A sample of tBPcLi$_2$ (75.2 mg, 0.100 mmol) was added, and the mixture was refluxed for 18 h. The mixture was cooled and concentrated. Chromatography (silica, $CHCl_3$ then $CHCl_3$/methanol (10:1)) gave one band (green) which was further purified by SEC (THF). Final purification on silica ($CHCl_3$) afforded a green solid (80.9 mg, 57%). LD-MS (*m*/*z*): obsd 1463.3, 1407.3, 1394.3. FAB-MS (*m*/*z*): obsd 1466.74, calcd 1466.74 ($C_{88}H_{100}N_{12}Ce$). λ_{abs}: 336, 402, 469, 586, 629 nm.

(tBPc)Ce(tBPc). A solution of $CeI[N(SiMe_3)_2]_2$, prepared in situ by reaction of CeI_3 (139.2 mg, 0.267 mmol) and $LiN(SiMe_3)_2$ (535 μL, 0.535 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (5 mL) following the standard procedure, was reacted with tBPcH$_2$ (51.1 mg, 67.1 μmol) at reflux for 20 h. The mixture was cooled, concentrated, and chromatographed (silica, $CHCl_3$ then $CHCl_3$/methanol (10:1)). The first band (blue, tBPcH$_2$) was not collected. The second band (green) was further purified by SEC (THF). The first band (green) was collected, affording a green solid (40.2 mg, 74%). Analytical data were consistent with the literature.[64]

[(octyloxy)$_8$Pc]$_2$Ce. A solution of $CeI[N(SiMe_3)_2]_2$, prepared by in situ reaction of CeI_3 (194.1 mg, 0.373 mmol) and $LiN(SiMe_3)_2$ (746 μL, 0.746 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (6 mL) following the standard procedure, was reacted with (octyloxy)$_8$PcH$_2$ (142.8 mg, 92.7 μmol) at reflux for 17 h. The mixture was cooled, concentrated, and chromatographed (silica, $CHCl_3$). The second band (green) was collected and further purified by SEC (THF). The second band (green) was collected, affording a green solid (98.8 mg, 66%). ^1H NMR: δ 0.96 (t, $J = 7.5$ Hz, 48H), 1.3−1.7 (m, 128H), 1.7−1.9 (m, 32H), 2.2 (dt, $J = 7.5$ Hz, $J = 6.6$ Hz, 32H), 4.5 (dt, $J = 8.1$ Hz, $J = 6.6$ Hz, 16H), 4.8 (dt, $J = 8.7$ Hz, $J = 6.0$ Hz, 16H), 8.4 (s, 16H). LD-MS (*m*/*z*): obsd 3212.0, 3172.6, 3102.2, 3002.6, calcd average mass 3216.56 ($C_{192}H_{288}N_{16}O_{16}Ce$). λ_{abs}: 358, 472, 644, 697 nm.

Exemplary Procedure for the Synthesis of a Cerium-Containing Triple Decker, Given for (TTP)Ce(tBPc)Ce(TTP). A solution of $CeI[N(SiMe_3)_2]_2$ was prepared in situ by reaction of CeI_3 (114 mg, 0.219 mmol) and $LiN(SiMe_3)_2$ (438 μL, 0.438 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (6 mL) following the standard procedure. Then a sample of *meso*-tetra-*p*-tolylporphyrin (36.7 mg, 0.055 mmol) was added and the mixture was refluxed for 3 h, affording the metalated porphyrin as determined by UV−vis spectroscopy. A sample of tBPcLi$_2$ (19.9 mg, 0.027 mmol) was added, and the mixture was refluxed for 18 h. The mixture was cooled and concentrated. Chromatography (silica, $CHCl_3$/methanol 10:1) gave one band (green) which was further separated by SEC (THF). The first brownish green band was collected and gave 12 mg after removal of the solvent. This material was suspended in methanol and filtered. The filtered material was taken up in CH_2Cl_2 and passed over a glass fiber filter. The filtrate was concentrated to give a brownish green solid (8.6 mg, 13%). LD-MS (POPOP) (*m*/*z*): obsd 2355.3, 1545.8, 808.5, 673.4. FAB-MS (*m*/*z*): obsd 2352.69, calcd 2352.80 ($C_{144}H_{120}N_{16}Ce_2$). λ_{abs}: 362, 422, 492, 607 nm. The second band from SEC gave the greenish double decker (TTP)Ce(tBPc) (17 mg, 41%).

(PnP)Ce(tBPc)Ce(PnP). A solution of $CeI[N(SiMe_3)_2]_2$, prepared in situ by reaction of CeI_3 (182 mg, 0.349 mmol) and $LiN(SiMe_3)_2$ (698 μL, 0.698 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (5 mL) following the standard procedure, was reacted with *meso*-tetrapentylporphyrin (30.4 mg, 51.4 μmol) at reflux for 3 h, affording the metalated porphyrin as determined by UV−vis spectroscopy. A sample of tBPcLi$_2$ (13.7 mg, 18.2 μmol) was added, and the mixture was refluxed for 18 h. The mixture was cooled and concentrated. Chromatography (silica, $CHCl_3$ then $CHCl_3$/methanol (10:1)) afforded one band (green) which was further separated by SEC (THF). The first brownish green band was collected and further purified by chromatography (silica, toluene), which afforded a brownish green solid (7.2 mg, 13%). ^1H NMR: δ −4.3 (br s, 16H), −2.2 to −2.0 (m, 8H), −2.0 to −1.8 (m, 36H), 0.6 (br s, 16H), 0.8−1.0 (m, 24H), 1.1−1.2 (m, 16H), 2.2 (s, 4H), 3.6 (br s, 16H), 3.7 (br s, 16H). LD-MS (POPOP) (*m*/*z*): obsd 2255.4, 2241.4, 2199.7, 2142.2, 2128.8, 1496.2. FAB-MS (*m*/*z*): obsd 2193.05, calcd 2193.05 ($C_{128}H_{152}N_{16}Ce_2$). λ_{abs}: 354, 426, 497, 568, 615 nm. The second band from SEC afforded the greenish double decker (PnP)Ce(tBPc) (12 mg, 45%).

(TTP)Ce(tBPc)Eu(tBPc). A solution of $CeI[N(SiMe_3)_2]_2$, prepared in situ by reaction of CeI_3 (106 mg, 0.204 mmol) and $LiN(SiMe_3)_2$ (408 μL, 0.408 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (5

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(64) Tomilova, L. G.; Chernykh, E. V.; Nikolaeva, T. B.; Zelentsov, V. V.; Luk'yanets, E. A. *Zh. Obshch. Khim.* **1984**, *54*, 1678−1679.

mL) following the standard procedure, was reacted with *meso*-tetra-*p*-tolylporphyrin (12.9 mg, 19.2 μmol) at reflux for 3 h, affording the metalated porphyrin as determined by UV−vis spectroscopy. The double-decker complex (tBPc)Eu(tBPc) (31.3 mg, 19.2 μmol) was added, and the mixture was refluxed for 18 h. The mixture was cooled and concentrated. Chromatography (silica, $CHCl_3$ then $CHCl_3$/methanol (10:1)) gave one band (green) which was further separated twice by SEC (THF). The product was dissolved in CH_2Cl_2 and filtered over a glass fiber filter. The filtrate was concentrated, affording a bluish green solid (24.8 mg, 53%). A ^{1}H NMR spectrum was collected, but the mixture of regioisomers made interpretation difficult. LD-MS (*m*/*z*): obsd 2438.1, 2424.0, 1629.0, 1549.4, 809.2. FAB-MS (*m*/*z*): obsd 2433.92, calcd 2433.92 ($C_{144}H_{134}N_{20}CeEu$). λ_{abs}: 346, 421, 534, 624, 714 nm.

(OEP)Ce(tBPc)Eu(tBPc). A solution of $CeI[N(SiMe_3)_2]_2$, prepared in situ by reaction of CeI_3 (69.5 mg, 0.133 mmol) and $LiN(SiMe_3)_2$ (267 μL, 0.267 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (4 mL) following the standard procedure, was reacted with octaethylporphyrin (11.7 mg, 21.9 μmol) at reflux for 2.5 h, affording the metalated porphyrin as determined by UV−vis spectroscopy. The double-decker complex (tBPc)Eu(tBPc) (36.0 mg, 22.1 μmol) was added, and the mixture was refluxed for 18 h. The mixture was cooled and concentrated. Chromatography (silica, $CHCl_3$ then $CHCl_3$/ethyl acetate (4:1)) gave a first band (red, $OEPH_2$) and a second band (green, (tBPc)Eu(tBPc)), which were not collected. The third band (blue) was further separated by SEC (THF), affording a blue solid (19.3 mg, 38%). A ^{1}H NMR spectrum was collected, but the mixture of regioisomers made interpretation difficult. LD-MS (*m*/*z*): obsd 2298.2, 1626.8, 1408.6, 670.8. FAB-MS (*m*/*z*): obsd 2297.56, calcd 2297.98 ($C_{132}H_{140}N_{20}CeEu$). λ_{abs}: 344, 400, 546, 628, 712 nm.

(TTP)Ce[(octyloxy)$_8$Pc]Eu[(octyloxy)$_8$Pc]. A solution of $CeI[N(SiMe_3)_2]_2$, prepared in situ by reaction of CeI_3 (53.1 mg, 0.102 mmol) and $LiN(SiMe_3)_2$ (204 μL, 0.204 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (4 mL) following the standard procedure, was reacted with *meso*-tetra-*p*-tolylporphyrin (17.1 mg, 25.5 μmol) at reflux for 3 h, affording the metalated porphyrin as determined by UV−vis spectroscopy. The double-decker complex [(octyloxy)$_8$Pc]Eu[(octyloxy)$_8$Pc] (29.8 mg, 9.2 μmol) was added, and the mixture was refluxed for 24 h. The mixture was cooled and concentrated. Chromatography (silica, hexane/ether (9:1) then hexane/ether (4:1)) gave a first band (red, $TTPH_2$) and a second band (brown, reduced form of the double decker), which were not collected. The third band (brown-green) was further separated by SEC (THF); from this the second band (green) was collected and further purified by chromatography (silica, hexane/ether (9:1)), affording an olive green solid (14.5 mg, 39%). ^{1}H NMR: δ 0.72 (t, $J = 7.2$ Hz, 24H), 0.8−1.0 (m, 32H), 0.99 (t, $J = 7.2$ Hz, 24H), 1.0−1.4 (m, 76H), 1.4−1.5 (m, 32H), 1.5−1.7 (m, 32H), 1.7−1.9 (m, 16H), 2.0−2.2 (m, 16H), 2.5−2.6 (m, 8H), 3.5−3.6 (m, 8H), 5.0−5.1 (m, 16H), 5.3−5.4 (m, 8H), 5.4−5.5 (m, 8H), 5.9−6.0 (m, 8H), 6.42 (brs, 8H), 11.19 (s, 8H). LD-MS (*m*/*z*): obsd 4038.4, 3828.3, 807.8; calcd average mass 4037.4 ($C_{240}H_{324}N_{20}O_{16}CeEu$). λ_{abs}: 371, 426, 538, 629, 669, 721 nm.

(PnP)Ce(tBPc)Eu(TTP). A solution of $CeI[N(SiMe_3)_2]_2$, prepared in situ by reaction of CeI_3 (105 mg, 0.202 mmol) and $LiN(SiMe_3)_2$ (404 μL, 0.404 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (5 mL) following the standard procedure, was reacted with *meso*-tetrapentylporphyrin (11.7 mg, 19.8 μmol) at reflux for 3 h, affording the metalated porphyrin as determined by UV−vis spectroscopy. The double-decker complex (TTP)Eu(tBPc) (29.0 mg, 18.6 μmol) was added, and the mixture was refluxed for 3.5 h. The mixture was cooled and concentrated. Chromatography (silica, $CHCl_3$ then $CHCl_3$/methanol (10:1)) gave one band (green), which was further separated by SEC (THF). The first band (brownish green) was further chromatographed (silica, $CHCl_3$). The product was dissolved in CH_2Cl_2 and filtered over a glass fiber filter. The filtrate was concentrated, affording a brownish green solid (24.2 mg, 53%). ^{1}H NMR: δ −0.7 to −0.5 (br s, 8H), 0−0.1 (m, 12H), 0.1−0.3 (m, 16H), 0.3−0.5 (m, 8H), 0.5−0.7 (m, 36H), 1.5 (s, 4H), 2.9 (s, 12H), 5.0−5.5 (m, 8H), 6.3−6.7 (m, 8H), 7.0−7.2 (m, 8H), 8.0 (s, 4H), 8.1 (d, 4H), 9.1 (d, 4H), 12.5 (br s, 4H), 13.3 (br s, 4H). LD-MS (POPOP) (*m*/*z*): obsd 2284.3, 2226.3, 2212.8, 2158.3. FAB-MS (*m*/*z*): obsd 2285.92, calcd 2285.94 ($C_{136}H_{140}N_{16}CeEu$). λ_{abs}: 360, 367, 421, 493, 607 nm.

(3-Por)Ce(tBPc)Eu(TTP). A solution of $CeI[N(SiMe_3)_2]_2$, prepared in situ by reaction of CeI_3 (125 mg, 0.240 mmol) and $LiN(SiMe_3)_2$ (481 μL, 0.481 mmol, 1 M in THF) in bis(2-methoxyethyl) ether (5 mL) following the standard procedure, was reacted with **3**-$PorH_2$ (41.4 mg, 47.9 μmol) at reflux for 3 h, affording the metalated porphyrin as determined by UV−vis spectroscopy. The double-decker complex (TTP)Eu(tBPc) (74.8 mg, 48.1 μmol) was added, and the mixture was refluxed for 18 h. The mixture was cooled and concentrated. Chromatography (silica, $CHCl_3$ then $CHCl_3$/methanol (10:1)) gave one band (green), which was further separated thrice by SEC (THF), affording a brownish green solid (44.2 mg, 36%). A ^{1}H NMR spectrum was collected, but the mixture of regioisomers made interpretation difficult. LD-MS (*m*/*z*): obsd 2548.3, 2424.5. FAB-MS (*m*/*z*): obsd 2559.72, calcd 2559.72 ($C_{147}H_{123}CeEuIN_{16}Si$). λ_{abs}: 364, 420, 493, 607 nm.

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Supporting Information Available: Figures giving absorption, LD-MS, and ^{1}H NMR spectra for each new sandwich complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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