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Article

Triple-Decker Sandwich Compounds Bearing Compact Triallyl Tripods for Molecular Information Storage Applications

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The design of redox-active molecules that afford multistate operation and high charge density is essential for molecular information storage applications. Triple-decker sandwich compounds composed of two lanthanide metal ions and three porphyrinic ligands exhibit a large number of oxidation states within a relatively narrow electrochemical window. High charge density requires a small footprint upon tethering triple deckers to an electroactive surface. All triple deckers examined to date for information storage have been tethered via the terminal ligand and have exhibited large footprints (∼670 Å^2). Five new homonuclear (Eu or Ce) triple deckers have been prepared (via statistical or rational methods) to examine the effect of tether attachment site on molecular footprint. Three triple deckers are tethered via the terminal ligand (porphyrin) or central ligand (porphyrin or imidazophthalocyanine), whereas two triple deckers each bear two tethers, one at each terminal ligand. The tether is a compact triallyl tripod. Monolayers of the triple deckers on Si(100) were examined by electrochemical and FTIR techniques. Each triple decker exhibited the expected four resolved voltammetric waves, owing to formation of the mono-, di-, tri-, and tetracations. The electrochemical studies of surface coverage (Γ, obtained by integrating the voltammetric waves) reveal that coverages approaching 10^{-10} mol cm^{-2}, corresponding to a molecular footprint of ∼170 Å^2, are readily achieved for all five of the triple deckers. The surface coverage observed for the tripodal functionalized triple deckers is approximately 4-fold higher than that obtained for monopodal-functionalized triple deckers (carbon, oxygen, or sulfur anchor atoms) attached to either Si(100) or Au(111). The fact that similar, relatively high, surface coverages can be achieved regardless of the location (or number) of the tripodal tether indicates that the tripodal functionalization, rather than the location of the tether, is the primary determinant of the packing density.

Introduction

Porphyrinic macrocycles combine with lanthanide metal complexes to form double-decker and triple-decker sandwich complexes.[1−3] The triple deckers exhibit a large number of oxidation states within a relatively narrow electrochemical window. Owing to the facile redox-active properties, triple deckers have been considered for use as charge-storage components in molecular information storage media.[4−12] Such an application typically requires attachment of the triple

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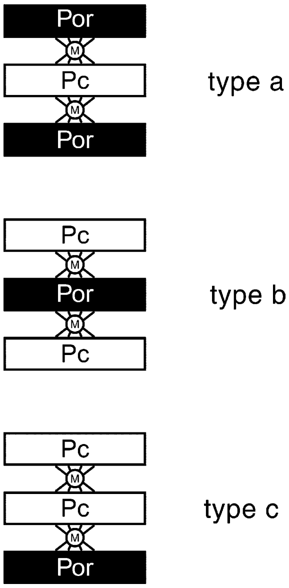

Figure 1. Structures of three types of heteroleptic triple-decker lanthanide sandwich complexes.

decker to an electroactive surface. The requirement for a covalent tether places constraints on the type of triple decker employed.

Three types of heteroleptic triple deckers composed of porphyrins and phthalocyanines are shown in Figure 1. Type-a [(Por)Ln(Pc)Ln(Por)], type-b [(Pc)Ln(Por)Ln(Pc)], and type-c [(Pc)Ln(Pc)Ln(Por)] triple deckers differ in the number and order of the respective porphyrin and phthalocyanine ligands. The term (Por) or (Pc) refers to the dianion of a generic porphyrin or phthalocyanine entity, respectively, in a sandwich architecture without regard to the nature of the substituents. We have almost exclusively employed type-c triple deckers in studies of molecular information storage. The choice of type-c triple deckers (which have one porphyrin and two phthalocyanine ligands) has stemmed from synthetic considerations, including (1) the existence of rational routes to type-a and type-c triple deckers,[13,14] whereas type-b triple deckers are only available by statistical reactions;[2−4] (2) the desire to incorporate a single tether; and (3) the greater sophistication of synthetic control in porphyrin versus phthalocyanine chemistry.[15] Indeed, 14 type-c triple deckers bearing tethers attached to the porphyrin ligand have been prepared.[4−6,8,10,11] Dyads and oligomers also have been prepared bearing one or two surface-attachment groups.[4,6,8,12] The surface-attachment groups have included aryl-SAc,[4,5] benzyl-SAc,[6,8,12] thiocyanate,[5] benzyl alcohol,[9,10] and tripodal benzyl-SAc.[11] The alcohol groups enable attachment to Si, whereas the thioacetate groups (which undergo deprotection in situ) enable attachment to Au or Si.

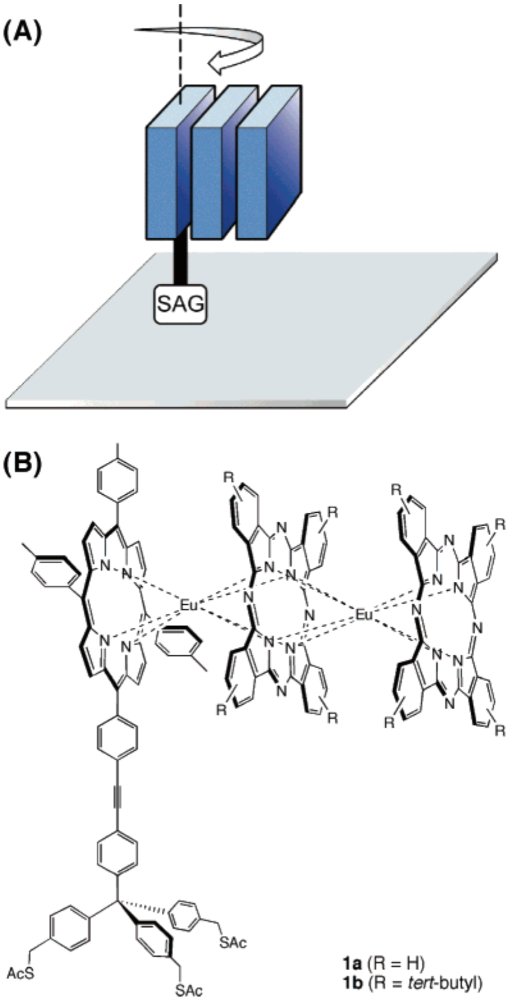

Figure 2. (A) Camshaft rotation of a type-c triple decker tethered to a surface (via a surface attachment group, denoted by “SAG”). (B) Examples of prior type-c triple deckers bearing tripodal tethers for surface attachment.

The triple-decker monomers exhibited a rather low surface coverage (2.5×10^{-11} mol cm^{-2}), corresponding to a large molecular footprint (∼670 Å^2).[8] Such a large area diminishes the surface charge density from the theoretical maximum. Achieving high surface charge density is a key objective of the molecular information storage approach. Because the tether is attached to the porphyrin, the triple decker in principle could rotate like a camshaft, sweeping out a large area (Figure 2A). In addition, the triple decker can tilt significantly on the surface (not shown). We felt that both the tilting and camshaft motions were the source of the substantial increase in molecular footprint and thereby diminished surface charge density. The use of a tripodal tether was examined in an effort to enforce a more upright orientation of the triple decker.[11] Two tripodal-substituted triple deckers were prepared (**1a** and **1b**, Figure 2B); however, each exhibited a surface coverage of $1{-}2 \times 10^{-11}$ mol cm^{-2}, which is still less dense than possible upon close packing. Two problems were apparent with this design: (1) the tri-thiol tripod itself exhibited a large footprint, and (2) the type-c triple decker could sweep out a large surface area by rotation about the tether axis.

To diminish the tripod footprint, we decided to use a compact triallyl tripod, which upon use with porphyrins has

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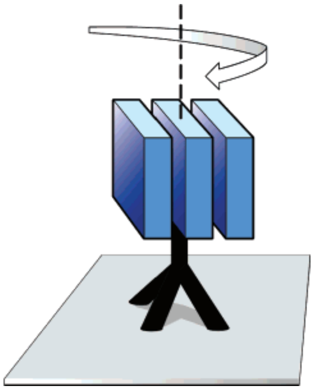
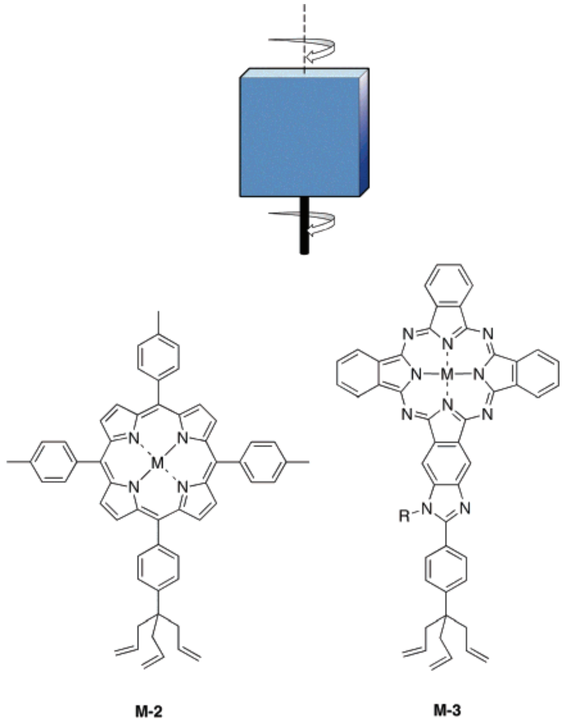


Figure 3. Centrally substituted triple decker bearing a tripodal tether. The tripod is attached to the phthalocyanine ligand in a type-a triple decker or to the porphyrin in a type-b triple decker.

afforded very close packing in self-assembled monolayers on Si(100).[16] To eliminate the camshaft rotation, we decided to prepare triple deckers bearing a tripodal tether attached to the central ligand, as illustrated in Figure 3. In principle, such a diametrically aligned triple decker can be obtained in two ways: (1) by use of a type-b triple decker where the tripodal tether is attached to the porphyrin or (2) by use of a type-a triple decker where the tripodal tether is attached to a phthalocyanine analogue. In both designs achieving axial pseudosymmetry of the triple decker requires that the tether axis bisect a C_2 axis of the porphyrin or phthalocyanine. Such symmetry is readily attained by substitution at the meso site of the porphyrin. For the phthalocyanine, each meso site is occupied by a nitrogen atom and is not available for substitution. Substitution at any of the benzo sites would afford a cant angle of the phthalocyanine, again resulting in a camshaft rotation of the corresponding triple decker with respect to the tether for surface attachment. We recently designed and synthesized phthalocyanines bearing 1−4 annulated imidazo units. Each annulated imidazo unit has two substituents: an *N*-imidazo substituent and a substituent at the imidazo 2-position. The substitution at the imidazo carbon results in an axial geometry that bisects an N−N axis of the macrocycle.[17] The porphyrin and phthalocyanine designs are shown in Figure 4. The free base porphyrin bearing the triallyl tripodal tether (**H_2-2**) has been synthesized previously.[16] The synthesis of the free base mono-imidazophthalocyanine (**H_2-3**) is described herein.

In this paper, we describe the synthesis of a set of triple-decker compounds bearing triallyl tripodal tethers and examination of their electrochemical and vibrational characteristics upon attachment to Si(100). The triple deckers are designed to explore the effect of site of attachment of the tether on the surface coverage and, hence, the charge density attainable for molecular information storage applications. Five triple deckers have been prepared, all of which are homonuclear (containing europium or cerium) and which contain one or two triallyl tethers. The triple deckers are as follows (1) type-c triple decker with a tether attached to the porphyrin, **(Pc)Eu(Pc)Eu(Por$^{\mathrm{Tpd}}$)**; (2) type-b triple decker with a tether attached to the porphyrin, **(Pc)Eu(Por$^{\mathrm{Tpd}}$)Eu(Pc)**; (3) type-a triple decker with a tether attached to the mono-imidazophthalocyanine, **(Por)Ce(Pc$^{\mathrm{Tpd}}$)Ce)(Por)**; (4) type-a triple decker with two tethers, one attached to each porphyrin, **(Por$^{\mathrm{Tpd}}$)Eu(Pc)Eu(Por$^{\mathrm{Tpd}}$)**; and (5) type-a triple decker with two tethers, **(Por$^{\mathrm{Tpd}}$)Ce(Pc)Ce(Por$^{\mathrm{Tpd}}$)**. The nontethered ligands include phthalocyanine (lacking any substituents) and *meso*-tetra-*p*-tolylporphyrin. The results from this study of the triple decker compounds provide insights into the design of surface-attached architectures for molecular information storage applications.



M-2 **M-3**

Figure 4. Tether attachment site affording a central axis of rotation in a porphyrin and an imidazophthalocyanine.

Results and Discussion

I. Synthesis. A. Methods of Triple-Decker Synthesis. The route to a given triple decker depends on the triple-decker type and the two metals in the sandwich complex. Homonuclear triple deckers of type a, type b, and type c can be obtained by statistical reaction wherein a free-base porphyrin is reacted with Ln(acac)$_3$•nH$_2$O in refluxing 1,2,4-trichlorobenzene followed by treatment with Li$_2$Pc. Purification of the resulting mixture of at least three distinct triple deckers (type a, type b, and type c) along with other double-decker species typically requires extensive chromatography. A rational route to type-c triple deckers (homonuclear or heteronuclear) entails the reaction of a free-base porphyrin with Ln(acac)$_3$•nH$_2$O or LnX$_3$/LiN(SiMe$_3$)$_2$ in THF to give the porphyrin−lanthanide half-sandwich complex, which is then treated with a double-decker phthalocyanine complex. A rational route to homonuclear type-a triple deckers entails the reaction of 2 equiv of a porphyrin−lanthanide half-sandwich complex with a dilithium phthalocyanine.[14] We are not aware of any rational routes to type-b triple deckers.

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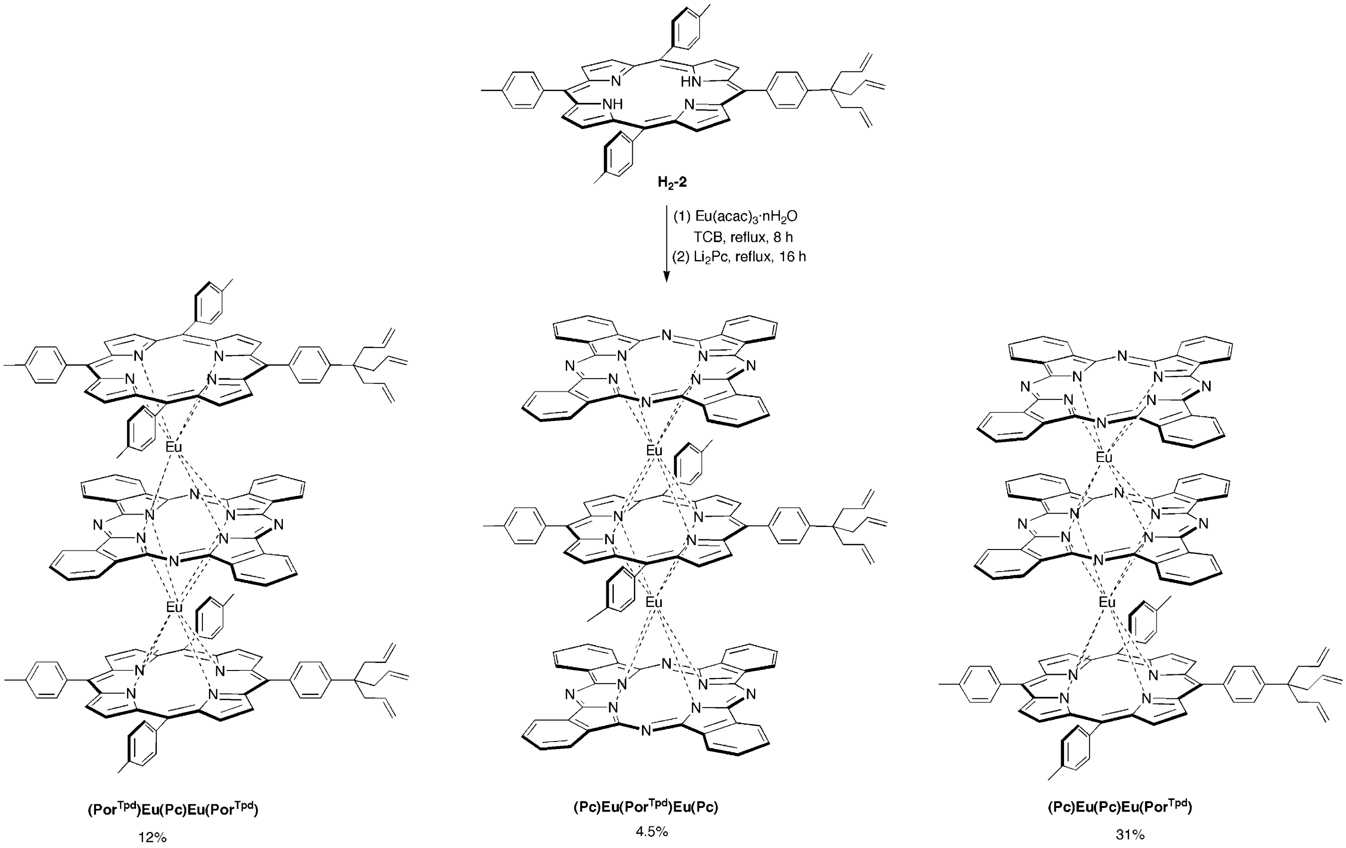
Scheme 1



The statistical route and the two rational routes were employed herein. Each triple decker was typically characterized by TLC analysis, UV−Vis absorption spectroscopy, ^{1}H NMR spectroscopy, laser-desorption mass spectrometry (LD-MS), and high-resolution mass spectrometry (FAB-MS or ESI-MS).

B. Europium Triple Deckers. 1. Statistical Route. The europium triple-decker sandwich complexes described herein were synthesized by the standard statistical method.[2,3] Thus, a mixture of tripodal-porphyrin **H$_2$-2** and excess Eu(acac)$_3$•nH$_2$O in 1,2,4-trichlorobenzene was refluxed to give the porphyrin half-sandwich complex (Por)Eu(acac). Upon use of 3 mol equiv of Eu(acac)$_3$•nH$_2$O, no reaction was observed even after 24 h of reflux. However, the addition of another portion of Eu(acac)$_3$•nH$_2$O (3 mol equiv) to the reaction mixture with continued reflux led to formation of the porphyrin half-sandwich complex within 2.5 h. Therefore, in subsequent reactions, we used 6 mol equiv of Eu(acac)$_3$•nH$_2$O.

The porphyrin half-sandwich complex was treated with Li$_2$Pc under reflux conditions (Scheme 1). TLC examination (silica, CH$_2$Cl$_2$) of the crude reaction mixture showed the presence of three major components, each corresponding to a triple decker: (1) component I, a yellowish green spot at $R_f = 0.92$; (2) component II, a black spot at $R_f = 0.34$; and (3) component III, a green spot at $R_f = 0.08$. Each of these products was isolated from the reaction mixture by column chromatography (silica, CH$_2$Cl$_2$) and characterized by ^{1}H NMR spectroscopy, LD-MS, and absorption spectroscopy. Component I was readily identified as the type-a triple decker **(Por^{Tpd})Eu(Pc)Eu(Por^{Tpd})** by LD-MS owing to the presence of two tethers, unlike type-b and type-c triple deckers, each of which contains only one tether. In addition, ^{1}H NMR spectroscopy showed the presence of two resonances (12.70 and 10.60 ppm), each with an integration of eight protons, owing to the α- and β-protons of the single phthalocyanine ring. The presence of the two resonances is consistent with rotation of the ligands with respect to each other about the central axis, a phenomenon that has been noted in other triple-decker complexes.[18]

Components II and III exhibited nearly identical molecule ion peaks, as expected for the isomeric type-b and type-c triple deckers. The ^{1}H NMR spectrum of component II showed two resonances (9.59 and 8.07 ppm), each with an integration of 16 protons, which can be assigned to the α- and β-protons of the two equivalent, outer phthalocyanine rings. By contrast, component III exhibited four resonances (12.85, 10.99, 9.95, and 8.61 ppm), each with an integration of eight protons, which can be assigned to the α- and β-protons of two distinct (inner and outer) phthalocyanine rings. Accordingly, component II is the type-b triple-decker **(Pc)Eu(Por^{Tpd})Eu(Pc)**, and component III is the type-c triple-decker **(Pc)Eu(Pc)Eu(Por^{Tpd})**. Chromatographic purification provided type-a (12%, 28.1 mg), type-b (4.5%, 18.4 mg), and type-c (31%, 129 mg) triple deckers.

2. Rational Route to Type-c Triple Decker. The type-c triple-decker **(Pc)Eu(Pc)Eu(Por^{Tpd})** also was synthesized

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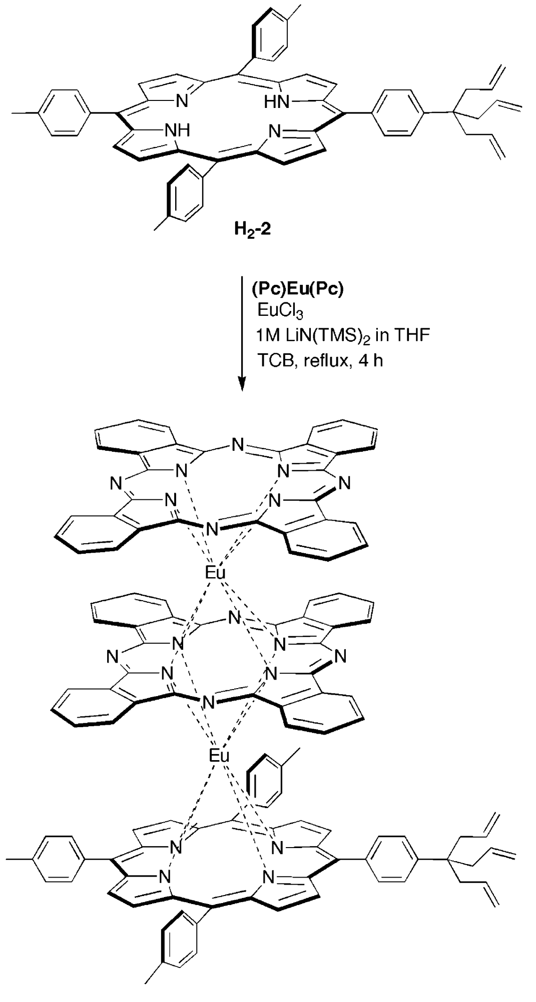
Scheme 2



(Pc)Eu(Pc)Eu(Por^{Tpd})
30%

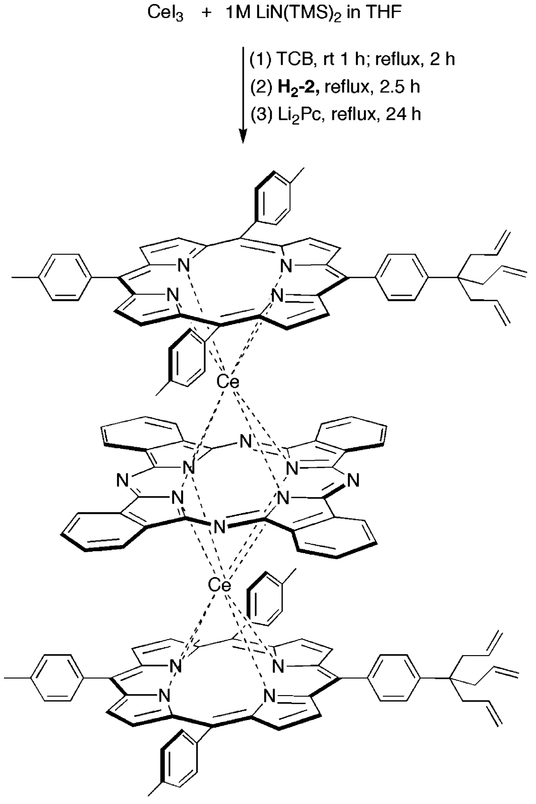
\+

(Por^{Tpd})Eu(Pc)Eu(Por^{Tpd})
trace

by a rational method (Scheme 2). This procedure entails treatment of the free-base porphyrin (**H$_2$-2**) with a double-decker sandwich complex [**(Pc)Eu(Pc)**] in the presence of EuCl$_3$/LiN(SiMe$_3$)$_2$ (1 M in THF) at 150 °C in 1,2,4-trichlorobenzene for 4 h. Chromatographic workup afforded type-c triple decker **(Pc)Eu(Pc)Eu(Por^{Tpd})** (30%, 63 mg), as well as a trace of the type-a triple decker. The characterization data obtained by ^{1}H NMR spectroscopy, LD-MS, and absorption spectroscopy were in agreement with those for **(Pc)Eu(Pc)Eu(Por^{Tpd})** prepared by the statistical method.

C. Cerium Triple Deckers. Lanthanide triple-decker sandwich coordination compounds generally afford four cationic oxidation states.[1] Cerium was chosen as the lanthanide metal in both layers of the triple decker because each cerium undergoes a further oxidation (Ce^{3+}/Ce^{4+}), affording a total of six cationic oxidation states.[19] The availability of six oxidation states is attractive for multibit storage in a given memory cell. Although we have prepared such homonuclear cerium-containing triple deckers,[14] all of the tethered triple deckers prepared to date have contained europium or europium/cerium.

Scheme 3



(Por^{Tpd})Ce(Pc)Ce(Por^{Tpd}) 6.4%

\+

(Pc)Ce(Por^{Tpd})Ce(Pc)
or 4%
(Pc)Ce(Pc)Ce(Por^{Tpd})

\+

(Por^{Tpd})Ce(Pc) 26%

1. Statistical Route. The synthesis of type-a, type-b, and type-c cerium triple deckers was carried out via the standard statistical method.[14] Accordingly, CeI[N(SiMe$_3$)$_2$] was prepared in situ by the treatment of CeI$_3$ with 2 mol equiv of LiN(SiMe$_3$)$_2$ (1 M in THF) in bis(2-methoxyethyl) ether. The reaction of CeI[N(SiMe$_3$)$_2$]$_2$ with the free-base tripodal porphyrin **H$_2$-2** (Ce/porphyrin ratio = 4:1) gave the corresponding porphyrin half-sandwich complex, (Por)CeX where X = I and/or N(SiMe$_3$)$_2$. The resulting solution of (Por)CeX was reacted with 2.2 mol equiv of Li$_2$Pc at reflux for 24 h. TLC examination (silica, CH$_2$Cl$_2$) of the crude reaction mixture showed three major components. Standard workup afforded component I (11.4 mg), component II (13 mg), component III (57 mg), and a trace amount of **(Por)Ce(Por)** (Scheme 3). Component I was readily identified as the type-a triple-decker **(Por^{Tpd})Ce(Pc)Ce(Por^{Tpd})** by LD-MS owing to the presence of two tripodal tethers, and component II was identified as the heteroleptic double-decker **(Por^{Tpd})-Ce(Pc).** Component III exhibited a molecule ion peak consistent with either a type-b or type-c triple decker,

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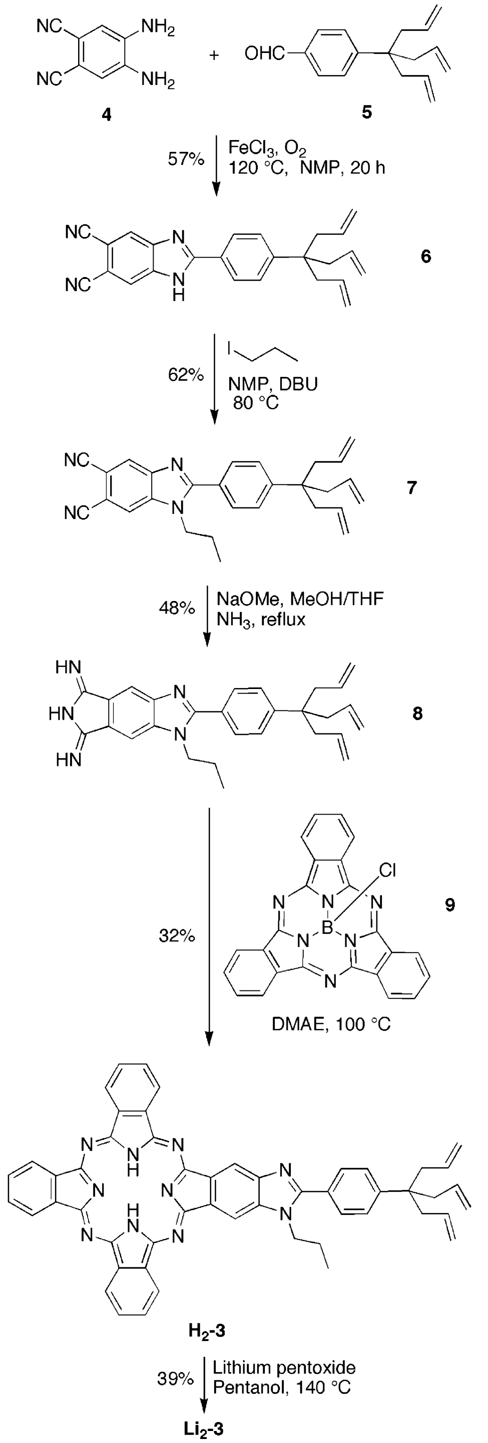
whereas the absorption spectrum more closely resembled that of the europium type-b versus type-c triple decker. The uncertain assignment precluded further study. The type-b triple decker **(Pc)Ce(Por^{Tpd})Ce(Pc)** was sought, owing to the presence of the tripodal tether on the central ligand. A centrally substituted all-cerium tripodal triple decker was obtained in unambiguous fashion by rational synthesis of a type-a triple decker bearing the tripodal tether on the phthalocyanine, as described in the next section.

2. Axially Aligned Tripodal-Phthalocyanine. The synthesis of the imidazophthalocyanine (**H$_2$-3**) bearing the tether at the 2-imidazo position and no substituents at the other benzo rings is best achieved by a ring-expansion reaction[20−24] of a subphthalocyanine and a benzimidazo-diiminoisoindoline. The incorporation of the triallyl tether via a *p*-phenylene unit at the 2-position of the imidazo unit required introduction of the tether at the earliest stage in the route to the diiminoisoindoline.

The reaction of dicyanophenylenediamine **4**[17] and a *p*-substituted benzaldehyde bearing the all-carbon tether (**5**)[16] proceeded via oxidative cyclization to form benzimidazole **6** in 57% yield (Scheme 4). The alkylation of **6** with 1-iodopropane afforded **7** in 62% yield accompanied by unreacted starting material (31% yield). The cyclization[25] of **7** afforded diiminoisoindoline **8** in 48% yield. The ring-expansion reaction[20−24] of subphthalocyanine **9**[26] was carried out using the polar, reducing solvent 2-dimethylaminoethanol (DMAE).[22] Due to the good reactivity of **8**, 4 equiv of **9** were required to suppress the formation of products bearing more than one imidazo moiety. After 8 h of reaction, the presence of reactant **9** was no longer evident and a substantial amount of unsubstituted phthalocyanine was formed in addition to the desired A$_3$B imidazophthalocyanine **H$_2$-3**. The purified **H$_2$-3** was treated with lithium pentoxide, smoothly affording the lithiated species **Li$_2$-3**. The product **Li$_2$-3** has greatly improved solubility compared to the free-base **H$_2$-3**, similar to that observed for lithium phthalocyanine.[27]

3. Rational Route to Type-a Triple Decker. The preparation of triple decker **(Por)Ce(Pc^{Tpd})Ce(Por)** was performed according to a procedure we previously reported.[14] Thus, CeI_3 in bis(2-methoxyethyl) ether was treated with $LiN(SiMe_3)_2$ at reflux, affording the putative I−Ce[N-$(SiMe_3)_2]_2$. The addition of tetra-*p*-tolylporphyrin (**H$_2$-10**) afforded the corresponding Ce−porphyrin half-sandwich complex, which was then treated with **Li$_2$-3** at reflux for 10 h (Scheme 5). Analytical SEC showed the absence of starting materials and the presence of a single triple decker. Purification by standard adsorption chromatography gave the triple decker in 30% yield. LD-MS analysis gave the expected molecule ion peak for the type-a triple decker **(Por)Ce-(Pc^{Tpd})Ce(Por)**. The ^{1}H NMR spectrum showed a complex and broadened signature due to the effects of the cerium atoms, but the resonances corresponding to the triallyl moiety were clearly defined and found in the same portion of the spectrum as for **H$_2$-3**. In summary, the rational synthesis of

Scheme 4



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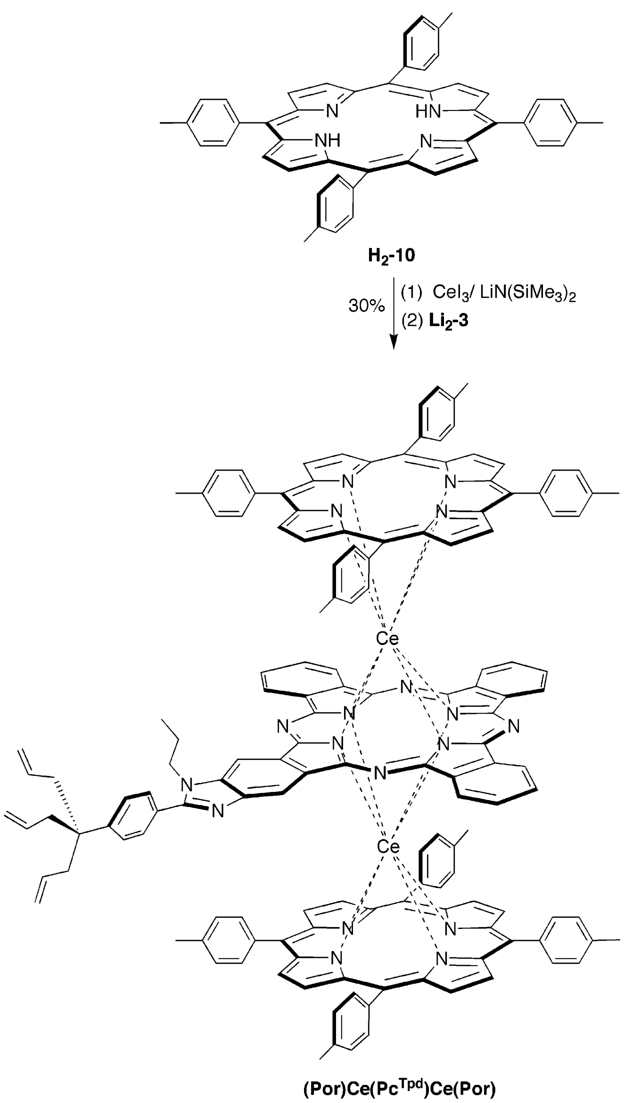
Scheme 5



triple decker **(Por)Ce(Pc^{Tpd})Ce(Por)** proceeded in a straightforward manner. The overall yield from the dicyanophenylenediamine **4** was low (0.6%), but valuable intermediates (**6**, **H$_2$-3**) could be recovered from two of the synthetic steps.

II. Monolayers on Si(100). A. Monolayer Characterization. Monolayers of the triple deckers were prepared on Si(100) substrates and examined via electrochemical and FTIR techniques. The monolayers were prepared on hydrogen-passivated Si(100) surfaces[28] by using a high-temperature (400 °C), 2-min "baking" procedure previously shown to give facile attachment of alkenyl functionalized porphyrins to Si(100) surfaces.[29] The general electrochemical characteristics of the triple-decker monolayers are similar to those we have previously reported for other types of triple deckers tethered to Si(100) or Au(111) via monopodal tethers.[7,8,10] Consequently, we will not reiterate these general features herein but rather only describe key features that distinguish the tripodal design from monopodal motifs. We also note that only the oxidative chemistry of the complexes was investigated herein. Although the triple deckers exhibit a number of reduced states,[5] the anions are not useful for information storage applications because anionic charges are difficult to maintain (in the absence of applied potential), owing to rapid neutralization even under highly inert conditions. The vibrational spectra of triple-decker monolayers have not been previously reported, and no detailed interpretation of the spectra is available (such an interpretation is outside the scope of this work). Accordingly, we focus our examination of the vibrational features on the most general characteristics of the spectra.

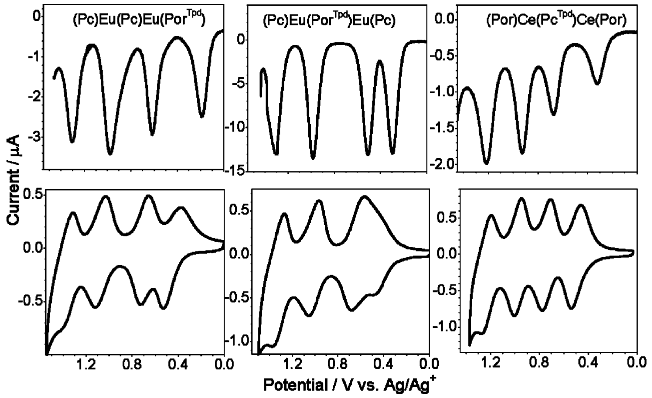


Figure 5. Voltammetry of the single-tether triple deckers in solution (top panels) and corresponding monolayers on Si(100) (bottom panels). Surface coverage: **(Pc)Eu(Pc)Eu(Por^{Tpd})**, $\Gamma \approx 6.3 \times 10^{-11}$ mol cm^{-2}; **(Pc)Eu(Por^{Tpd})Eu(Pc)**, $\Gamma \approx 7.5 \times 10^{-11}$ mol cm^{-2}; **(Por)Ce(Pc^{Tpd})Ce(Por)**, $\Gamma \approx 7.3 \times 10^{-11}$ mol cm^{-2}. The solution and monolayer data were obtained using square-wave voltammetry (0.1 V s^{-1}) and fast-scan cyclic voltammetry (100 V s^{-1}), respectively.

B. Electrochemical Studies of Surface Coverage, Electron-Transfer Rates, and Charge-Retention Times. The goal of the electrochemical studies was to determine the saturation surface coverage and elucidate the electron-transfer and charge-retention characteristics of the triple-decker monolayers. These properties of the monolayers are described below.

Representative fast scan (100 V s^{-1}) cyclic voltammograms for the single- and double-tether triple-decker monolayers on Si(100) microelectrodes (100 μm × 100 μm) are shown in Figures 5 and 6, respectively. For comparison, the voltammetric data for the parent triple deckers in solution are also shown in the figures. In the window 0−1.5 V, the monolayers exhibit four resolved voltammetric waves indicative of formation of the mono-, di-, tri-, and tetracations. The redox behavior of the monolayers parallels that of the parent molecules in solution. It should be noted that additional redox waves are observed for the triple deckers in solution at potentials above 1.5 V. These states cannot be accessed for the monolayers because surface oxidation occurs at these higher potentials, obscuring the voltammetric waves of the triple decker. The redox potentials for the triple deckers in solution and the monolayers are summarized in Table 1. Inspection of these data shows that the potentials for the monolayers are systematically shifted to higher values than those observed in solution, a characteristic similar to that

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(29) Liu, Z.; Yasseri, A. A.; Loewe, R. S.; Lysenko, A. B.; Malinovskii, V. L.; Zhao, Q.; Surthi, S.; Li, Q.; Misra, V.; Lindsey, J. S.; Bocian, D. F. *J. Org. Chem.* **2004**, *69*, 5568−5577.

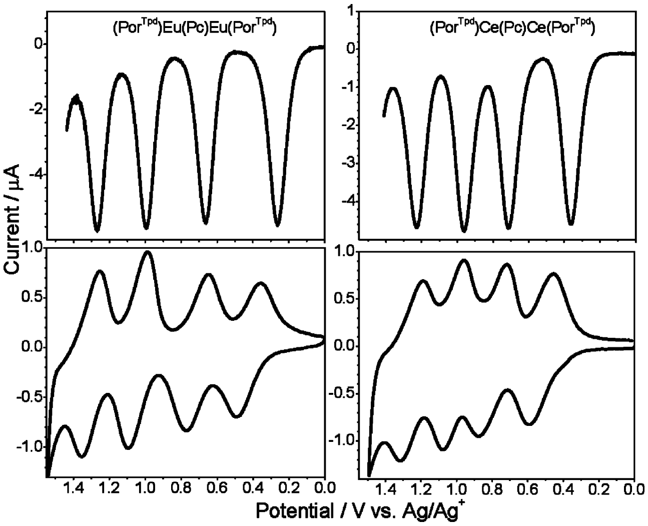

Figure 6. Voltammetry of the double-tether triple deckers in solution (top panels) and corresponding monolayers on Si(100) (bottom panels). Surface coverage: **(Por$^{\mathrm{Tpd}}$)Eu(Pc)Eu(Por$^{\mathrm{Tpd}}$)**, $\Gamma \approx 8.0 \times 10^{-11}$ mol cm^{-2}; **(Por$^{\mathrm{Tpd}}$)Ce(Pc)Ce(Por$^{\mathrm{Tpd}}$)**, $\Gamma \approx 8.9 \times 10^{-11}$ mol cm^{-2}. The solution and monolayer data were obtained using square-wave voltammetry (0.1 V s^{-1}) and fast-scan cyclic voltammetry (100 V s^{-1}), respectively.

observed for other tetrapyrrolic molecules in monolayers versus solution.[4−7,28]

One perhaps unexpected feature of the redox behavior of the different triple deckers is that the electrochemistry of all five complexes is generally similar. No clear trends are observable that can be related to the number or sequence of porphyrins versus phthalocyanines in the complex or the nature of the lanthanide. The similar redox chemistry of the Ce and Eu complexes is particularly surprising given that the Ce(III) ion can be oxidized in this potential region. The stability of the different triple deckers under successive redox cycling (at 100 V s^{-1}) is also quite similar. Monolayer integrity is maintained over thousands of cycles if the electrochemical window includes only the first or second waves but only over hundreds of cycles if the window is extended to include all four waves.

The electrochemical studies of surface coverage (Γ, obtained by integrating the voltammetric waves) reveal that coverages approaching 10^{-10} mol cm^{-2}, corresponding to a molecular footprint of ~170 Å^2, are readily achieved for all five of the triple deckers studied. The surface coverage observed for the tripodal functionalized triple deckers is approximately 4-fold higher than that obtained for monopodal-functionalized triple deckers (carbon, oxygen, or sulfur anchor atoms) attached to either Si(100) or Au(111).[7,8,10] The fact that similar, relatively high, surface coverages can be achieved regardless of the location (or number) of the tripodal tether indicates that the tripodal functionalization, rather than the location of the tether, is the primary determinant of the packing density. In this regard, we have previously found that tripodal-functionalized monomeric porphyrins exhibit much higher packing densities than do monopodal functionalized porphyrins.[16]

The standard electron-transfer rate constants, k^0, were measured for the first two oxidation processes ($E^{0/+1}$ and $E^{+1/+2}$) of the triple-decker monolayers at several different surface coverages from the low 10^{-12} to mid 10^{-11} mol cm^{-2} range; these rates are listed in Table 2. The interest in this surface-coverage dependence of the electron-transfer rates stems from our previous studies on porphyrin monolayers, both on Si(100) and Au(111), which show that the electron-transfer rates depend on surface coverage.[7,11,16,28,30,31] As we have previously discussed, the electron-transfer rates cannot be measured at very high surface concentrations, i.e., those near saturation coverages, owing to experimental limitations. Nevertheless, the available surface-coverage range is wide enough to compare the trends observed for the triple-decker monolayers. Inspection of the data presented in Table 2 reveals that the electron-transfer rate for all of the triple deckers are similar to one another and that these rates decrease with increasing surface coverage, similar to the behavior observed for other types of porphyrin monolayers on both Au(111) and Si(100).[7,11,16,28,30,31] In addition, the electron-transfer rates observed for the tripodal-functionalized triple deckers on Si(100) at a particular surface coverage are comparable to those observed for a monopodal-thiol-functionalized triple decker on Au(111).[7]

The charge-retention half-lives, $t_{1/2}$, were also measured at selected surface coverages for the first and second oxidation states of the triple-decker monolayers, in parallel with the studies of the electron-transfer kinetics; these times are reported in Table 2. Again, the interest in this surface-concentration dependence of charge-retention stems from our previous studies on porphyrin monolayers, both on Si(100) and Au(111), which show that this process also depends on surface coverage.[7,11,16,28,31] We were particularly interested in the charge-retention characteristics of the triple deckers at high surface coverage, beyond that achievable for porphyrins with monopodal linkers. Inspection of the data reported in Table 2 reveals that the charge-retention times for all of the monolayers increase (charge-dissipation rates decrease) as the surface concentration increases, consistent with previous observations on other types of porphyrin monolayers on both Au(111) and Si(100).[7,11,16,28,32] The charge-retention times for the triple deckers at surface concentrations in the low 10^{-11} mol cm^{-2} regime are in the sub-30 s range, comparable to those observed for analogous triple deckers with monopodal tethers.[7,8,10] As the surface coverage is increased toward the 10^{-10} mol cm^{-2} range, the charge-retention times increase to over 100 s.

C. FTIR Studies of Surface-Attachment Motif. The electrochemical studies show that the tripodal tether affords significantly higher surface coverage for the triple deckers than does a monopodal tether. To explore the surface-binding motif of the tripodal functionalized triple deckers, we examined these monolayers using FTIR spectroscopy. The mid-frequency (700−1900 cm^{-1}) IR spectra of the single- and double-tether triple deckers are shown in Figures 7 and 8, respectively; the spectrum of solid samples of each parent porphyrin are also shown. The IR spectra of a given triple decker in the monolayer and solid forms are generally similar to one another, indicating that the structure of the triple decker is relatively unperturbed upon surface attachment (as

Table 1. Half-Wave Potentials for the Triple Deckers in Solution and the Corresponding Monolayers[a] on Si(100)

	half-wave potential							
	$E^{0/+1}$		$E^{+1/+2}$		$E^{+2/+3}$		$E^{+3/+4}$	
triple decker	soln	monolayer	soln	monolayer	soln	monolayer	soln	monolayer
(Pc)Eu(Pc)Eu(Por^{Tpd})	0.18	0.44	0.60	0.69	0.97	1.08	1.29	1.33
(Pc)Eu(Por^{Tpd})Eu(Pc)	0.30	0.40[b]	0.50	0.63[b]	0.98	1.02	1.30	1.30
(Por)Ce(Pc^{Tpd})Ce(Por)	0.32	0.49	0.67	0.74	0.93	0.97	1.21	1.23
(Por^{Tpd})Eu(Pc)Eu(Por^{Tpd})	0.26	0.42	0.67	0.72	0.99	1.05	1.26	1.29
(Por^{Tpd})Ce(Pc)Ce(Por^{Tpd})	0.36	0.52	0.71	0.79	0.96	1.04	1.23	1.25

[a] Surface coverage: **(Pc)Eu(Pc)Eu(Por^{Tpd})**, $\Gamma \approx 6.3 \times 10^{-11}$ mol cm^{-2}; **(Pc)Eu(Por^{Tpd})Eu(Pc)**, $\Gamma \approx 7.5 \times 10^{-11}$ mol cm^{-2}; **(Por)Ce(Pc^{Tpd})Ce(Por)**, $\Gamma \approx 7.3 \times 10^{-11}$ mol cm^{-2}; **(Por^{Tpd})Eu(Pc)Eu(Por^{Tpd})**, $\Gamma \approx 8.0 \times 10^{-11}$ mol cm^{-2}; **(Por^{Tpd})Ce(Pc)Ce(Por^{Tpd})**, $\Gamma \approx 8.9 \times 10^{-11}$ mol cm^{-2} [$\Gamma = \sigma/eN_A$, where σ is the charge density, e is the charge of the electron, and N_A is Avogadro's number]. [b] These two redox waves are highly overlapped, and the E values were determined by deconvolution.

Table 2. Surface Coverage (Γ), Dependence of the Electron-Transfer Rates (k^0), and Charge-Retention Half-Lives ($t_{1/2}$) for the Triple Deckers on Si(100)

		state 1		state 2	
triple decker	Γ ($\times 10^{-11}$ mol cm^{-2})	k^0 ($E^{0/+1}$) ($\times 10^4$ s^{-1})	$t_{1/2}$ ($E^{+1/0}$) (s)	k^0 ($E^{+1/+2}$) ($\times 10^4$ s^{-1})	$t_{1/2}$($E^{+2/0}$)[a] (s)
(Pc)Eu(Pc)Eu(Por^{Tpd})	0.4	3.0	10	2.7	15
	2.2	1.0	22	0.9	30
	4.7	*b*	63	*b*	70
(Pc)Eu(Por^{Tpd})Eu(Pc)	0.7	3.0	15	2.8	26
	3.1	0.8	46	0.8	70
	7.7	*b*	96	*b*	106
(Por)Ce(Pc^{Tpd})Ce(Por)	0.33	3.6	12	3.0	15
	2.8	1.1	46	1.0	53
	12	*b*	110	*b*	120
(Por^{Tpd})Eu(Pc)Eu(Por^{Tpd})	0.5	2.9	15	2.6	21
	2.7	0.9	24	0.8	40
	6.2	*b*	83	*b*	100
(Por^{Tpd})Ce(Pc)Ce(Por^{Tpd})	0.7	2.8	28	2.5	32
	3.0	0.8	45	0.7	70
	8.8	*b*	111	*b*	123

[a] Note that this $t_{1/2}$ value corresponds to loss of 2 equiv of charge. [b] Not determined (see text).

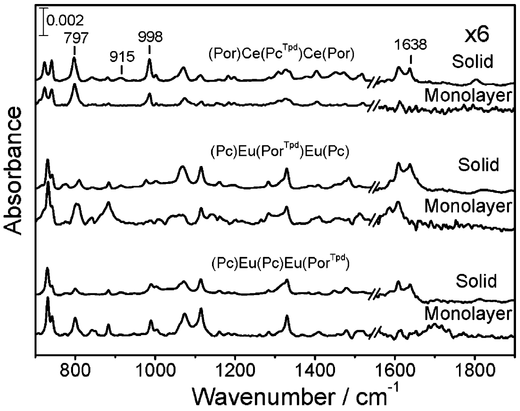

Figure 7. FTIR spectra of the single-tether triple deckers in solid form (KBr) and the corresponding monolayers on Si(100).

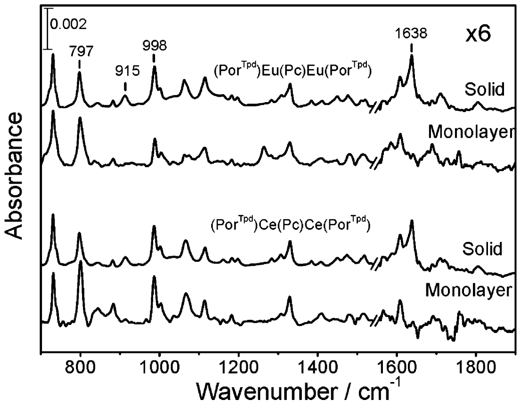

Figure 8. FTIR spectra of the double-tether triple deckers in solid form (KBr) and the corresponding monolayers on Si(100).

expected[11,16,30,31]). Two key features observed in the spectra of the solids are the C=C stretching vibration, ν(C=C), of the alkene group in the tripodal linker at 1638 cm^{-1} and out-of-plane C−H deformation, γ(CH), of this group at 915 cm^{-1}.[33] Comparison of the IR spectra of the solid and monolayers reveals that the bands due to the ν(C=C) (1638 cm^{-1}) and γ(CH) (915 cm^{-1}) vibrations are absent from the spectra of the monolayers. The absence of these bands is consistent with saturation of the double bond in each of the three legs of the tripod. These data are consistent with, although not definitive proof of, the view that each of the three legs of the compact tripod attaches to the Si(100) surface via a hydrosilylation reaction (as expected when an

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alkene reacts with hydrogen-passivated silicon[34]). The absence of the ν(C=C) (1638 cm^{-1}) and γ(CH) (915 cm^{-1}) bands for the double-tether triple deckers is further consistent with the view that the molecule is bound to the Si(100) surface via both linkers. Attachment of both tethers of a given triple decker is consistent with the observations of rotation of the ligands with respect to each other about the central axis, thereby enabling the two tethers to contact the surface.

Outlook

We began the studies reported herein with the conviction that placing the tether at the center of the triple decker rather than at the terminal ligand would eliminate the camshaft rotation and thereby afford a smaller footprint. To our surprise, we found that the use of a compact triallyl tripod suffices to give substantial increases in surface packing density (affording a footprint of ~170 Å^2) regardless of the ligand to which the tether is attached. The extent to which even smaller footprints can be obtained is not clear. Regardless, the closer packing obtained with the triallyl tripod makes triple deckers more attractive for molecular information storage applications. The ability to attach the triallyl tether at a variety of sites also facilitates synthetic design: rational syntheses provide access to a type-c triple decker bearing the tether on the porphyrin or a type-a triple decker bearing the tether on an imidazophthalocyanine. Alternatively, statistical synthesis provides access to a type-b triple decker bearing the tether on the porphyrin.

The small footprint achievable by monomeric porphyrins (~75 Å^2) on an electroactive surface has afforded charge densities (43 μC cm^{-2}) that are substantially greater than those of typical semiconductor materials (~1−2 μC cm^{-2}) employed as charge-storage media in memory applications.[16,35] Triple-decker sandwich compounds offer multistate features that are not available with porphyrin monomers, but heretofore, the increased number of states has come at the expense of a substantial decrease in charge density. Indeed, the ability to store four charges in a triple decker with the previously obtained footprint of ~670 Å^2 is not comparable to two charges in a porphyrin with a footprint of ~75 Å^2. Retaining high charge density is a key design objective in molecular information storage. The tripod used in the present studies affords a molecular footprint of ~170 Å^2 for all five of the triple deckers. The studies reported herein further suggest that the number and sequence of the porphyrins versus phthalocyanines in the complex and the nature of the lanthanide do not have much affect on the features that are required for the complex to serve as a viable molecular information storage medium.

Experimental Section

I. General Methods. A. Solvents and Reagents. Solvents including MeOH (anhydrous), CH_2Cl_2, $CHCl_3$ (stabilized with 0.8% EtOH), *N*-methyl pyrrolidinone (NMP, anhydrous), and DMAE (redistilled grade) were reagent grade and were used as received. THF was freshly distilled from sodium/benzophenone as required. Toluene was distilled from CaH_2. Purified acetone was prepared from reagent grade acetone by distillation over potassium permanganate and storing the distillate over anhydrous K_2CO_3 prior to use. NaOMe was employed as a 25 wt % solution in MeOH. All other chemicals were reagent grade and were used as received.

B. Chromatography. Analytical size exclusion chromatography (SEC) was performed on an HPLC instrument using one 1000 Å column (5 μL, styrene−divinylbenzene copolymer) with THF as eluent (flow rate 0.8 mL min^{-1}; oven temperature 20 °C). Preparative-scale SEC was performed using BioRad Bio-beads SX-1 or SX-3 in THF.[4,6] Silica gel (40 μm average particle size) was used for column chromatography.

C. Characterization. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained in $CDCl_3$ unless noted otherwise. Mass spectra were obtained via laser desorption mass spectrometry (LD-MS) without a matrix[36] or by matrix-assisted laser desorption ionization mass spectroscopy (MALDI-MS), by high-resolution fast atom bombardment mass spectrometry (FAB-MS) using a matrix of nitrobenzyl alcohol and poly(ethylene glycol), or by ESI-MS. Triple deckers often present challenges to high-resolution mass spectral methods, owing to limited volatility and solubility; the deviations from the exact mass observed herein reached as high as 44 ppm. Absorption and emission data were measured in THF unless noted otherwise. The fluorescence quantum yield of **H_2-3** was measured by comparison to tetra-*tert*-butylphthalocyanine (reported[37] $\Phi_f = 0.77$ in $CHCl_3$; determined herein in THF to be $\Phi_f = 0.70$) with corrected integrated emission spectra and refractive index corrections. Melting points are uncorrected.

D. Noncommercial Compounds. Compounds **H_2-2**,[16] **4**,[17] **5**,[16] **9**,[26] and **(Pc)Eu(Pc)**[14] were prepared according to the literature.

II. Synthetic Procedures. A. Statistical Synthesis of Europium Triple Deckers. Following a standard procedure,[2−4] the free-base porphyrin tripod **H_2-2** (153 mg, 194 μmol) in 1,2,4-trichlorobenzene (38 mL) was treated with Eu(acac)$_3$·nH$_2$O (573 mg, 1.16 mmol, 6 equiv) at reflux. The reaction was monitored by absorption spectroscopy for the absence of the peak at 650 nm (characteristic of the free-base porphyrin) to ensure complete formation of the porphyrin−europium half sandwich complex. The reaction was stopped after 8 h and allowed to cool long enough for the refluxing to subside and to enable the addition of Li_2Pc. A sample of Li_2Pc (205 mg, 389 μmol) was added, and heating was continued at reflux. The reaction was monitored by TLC analysis. The reaction was stopped after 16 h. The reaction mixture was filtered, and the residue was rinsed with CH_2Cl_2. The rinsings were combined with the filtrate. The solvent was removed under reduced pressure to provide the crude reaction mixture, which upon TLC examination (silica, CH_2Cl_2) showed the presence of three major components: (1) component I, a yellowish green spot at $R_f = 0.92$; (2) component II, a black spot at $R_f = 0.34$; and (3) component III, a green spot at $R_f = 0.08$. The crude mixture was chromatographed (silica, CH_2Cl_2). Each of the components was isolated and characterized by ^{1}H NMR spectroscopy, LD-MS, and absorption spectroscopy. Characterization and analysis revealed that component I is the type-a triple-decker **(Por^{Tpd})Eu(Pc)Eu(Por^{Tpd})**, component II is the type-b triple-decker **(Pc)Eu(Por^{Tpd})Eu(Pc)**, and component III is the

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[34] (a) Buriak, J. M. *Chem. Commun.* **1999**, 1051−1060. (b) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271−1308.

[35] Thamyongkit, P.; Yu, L.; Padmaja, K.; Jiao, J.; Bocian, D. F.; Lindsey, J. S. *J. Org. Chem.* **2006**, *71*, 1156−1171.

[36] (a) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **1997**, *1*, 93−99. (b) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 283−291.

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type-c triple-decker **(Pc)Eu(Pc)Eu(Por^{Tpd})**. The detailed purification procedure is described below.

The isolated type-a triple decker from the first silica column was washed with methanol and hexanes. This washing procedure involves dissolving the compound in CH_2Cl_2 and adding an equal volume of methanol. Slow rotary evaporation afforded a suspension to which additional methanol was added. The mixture was sonicated and centrifuged, and the supernatant was removed. The process of suspending the residue, sonication followed by centrifugation and removal of the supernatant, was repeated once more in methanol and twice in hexanes. The residue thus obtained was thoroughly dried under vacuum and characterized. This procedure provided triple-decker type-a (8.5 mg, 3.7%). Another fraction containing triple-decker type-a along with other impurities collected from the first column was subjected to further purification by a second column [silica gel, hexanes/ethyl acetate (95:5)] providing an additional 20 mg (8.4%) along with an impure fraction of 74 mg (∼80% purity). Thus, the combined isolated yield of type-a triple decker was 12%.

The isolated type-b triple decker from the first silica column was washed with methanol and hexanes in the manner described above, providing 8.6 mg (2.1%). Another fraction containing triple-decker type-b with other impurities collected from the first column was subjected to further purification by a second column (silica gel, CH_2Cl_2), providing an additional 9.8 mg (2.4%). Thus, the combined isolated yield of type-b triple decker was 4.5%.

The type-c triple decker was isolated in 31% yield (129 mg) from the first silica column along with an impure fraction (9.3 mg, >95% purity).

The characterization data for each of these triple deckers are given below.

(Por^{Tpd})Eu(Pc)Eu(Por^{Tpd}). Yield (28.5 mg, 12%); ^{1}H NMR 2.87−2.99 (m, 18H), 2.99−3.10 (m, 12H), 3.81−4.04 (m, 16H), 4.63−4.93 (m, 8H), 5.45−5.59 (m, 12H), 6.11−6.30 (m, 6H), 6.42−6.61 (m, 6H), 6.61−6.71 (m, 2H), 8.74−8.92 (m, 6H), 8.95−9.07 (m, 2H), 10.60 (br, 8H), 11.40−11.80 (m, 8H), 12.70 ppm (br, 8H); LD-MS obsd 2394.1; ESI-MS obsd 2395.6694, calcd 2395.7759 [(M + H)$^+$; M = $C_{146}H_{112}Eu_2N_{16}$]; λ_{abs} (toluene) 355, 421, 492, 607 nm.

(Pc)Eu(Por^{Tpd})Eu(Pc). Yield (18.4 mg, 4.5%); ^{1}H NMR (300 MHz) 4.00−4.21 (m, 15H), 6.12−6.32 (m, 6H), 7.12−7.34 (m, 3H, merged with chloroform peak), 8.07 (br, 16H), 9.59 (br, 16H), 9.70−10.0 (m, 6H), 10.0−10.2 (m, 2H), 11.78−12.08 (m, 6H), 12.08−12.25 (m, 2H), 13.50−13.58 (m, 4H), 13.58−14.08 ppm (m, 4H); LD-MS obsd 2119.1; ESI-MS obsd 2118.4751, calcd 2118.5300 ($C_{121}H_{80}Eu_2N_{20}$); λ_{abs} (toluene) 343, 445, 517, 652, 788 nm.

(Pc)Eu(Pc)Eu(Por^{Tpd}). Yield (129 mg, 31%); ^{1}H NMR (300 MHz) 2.84−3.34 (m, 23H), 4.70−5.0 (m, 4H), 5.42−5.64 (m, 6H), 6.1−6.24 (m, 3H), 6.42−6.70 (m, 4H), 8.61 (br, 8H), 8.80−9.22 (m, 4H), 9.95 (br, 8H), 10.99 (br, 8H), 11.80−12.18 (m, 4H), 12.85 ppm (br, 8H); LD-MS obsd 2118.9; ESI-MS obsd 2119.5127, calcd 2119.5378 [(M + H)$^+$; M = $C_{121}H_{80}Eu_2N_{20}$]; λ_{abs} (toluene) 342, 415, 521, 553, 619, 721 nm.

B. Rational Synthesis of Type-c Europium Triple Decker. Following a rational method[14] with slight modifications (Padmaja, K.; Lysenko, A.; Loewe, R. S.; Lindsey, J. S., unpublished), a mixture of free-base porphyrin bearing the triallyl tripod **H$_2$-2** (79.1 mg, 0.100 mmol) and **(Pc)Eu(Pc)** (118 mg, 0.100 mmol) in TCB (3.4 mL) was treated with $EuCl_3$ (206 mg, 0.800 mmol) and $LiN(SiMe_3)_2$ (1.60 mL, 1.60 mmol, 1M in THF). The reaction mixture was gradually heated to 150 °C over a period of 30 min and stirred at 150 °C. The reaction was stopped after 4 h. TLC examination of the reaction mixture showed the presence of type-a and type-c triple deckers. The reaction mixture was filtered, and the residue was rinsed with CH_2Cl_2. The rinsings were combined with the filtrate. The solvent was removed under reduced pressure to provide the crude reaction mixture, which was chromatographed (silica gel, CH_2Cl_2) to provide the desired type-c triple decker (green) (63 mg, 30%) along with another fraction (12 mg, >95% purity). The characterization data were consistent with those for the product obtained from the statistical synthesis. TLC examination of the reaction mixture revealed the formation of a trace amount of type-a triple decker.

C. Statistical Synthesis of Cerium Triple Deckers. Following a standard procedure,[14] a mixture of CeI_3 (313 mg, 0.600 mmol) in bis(2-methoxyethyl) ether (30 mL) in a 100 mL Schlenk flask at 0 °C was treated dropwise with $LiN(SiMe_3)_2$ (1.20 mL, 1.20 mmol, 1M in THF). Stirring was continued while the mixture was warmed to room temperature (ca. 1 h). The reaction mixture was gradually heated to reflux (∼170 °C oil bath temperature) over a period of ∼20 min. The reflux was continued for 2 h during which the cerium beads reacted. Then, free-base porphyrin **H$_2$-2** (119 mg, 0.150 mmol) was added and the mixture was refluxed. The reaction was monitored by absorption spectroscopy for the complete consumption of the free-base porphyrin. The reaction was stopped after 2.5 h and allowed to cool long enough for the refluxing to subside to enable addition of Li_2Pc. A sample of Li_2Pc (173 mg, 0.330 mmol) was added, and heating was continued to reflux. The reaction was stopped after 24 h. The reaction mixture was cooled to room temperature and filtered. The residue was rinsed with CH_2Cl_2. The rinsings were combined with the filtrate. The solvent was removed under reduced pressure to provide the crude reaction mixture, which upon TLC examination (silica, CH_2Cl_2) showed three major components: (1) component I, a yellowish green spot at $R_f = 0.9$; (2) component II, a green spot at $R_f = 0.66$; and (3) component III, a green spot at $R_f = 0.28$, along with other minor products. The reaction mixture thus obtained was chromatographed (silica gel, CH_2Cl_2). Five bands were collected, the homoleptic porphyrin double-decker **(Por^{Tpd})Ce(Por^{Tpd})** (first band; minor; purple), unreacted starting porphyrin (second band; minor; purple), type-a triple decker (third band; yellowish green), heteroleptic double-decker **(Por^{Tpd})Ce(Pc)** (fourth band; green), and type-b/c triple decker (unidentified as to type-b or type-c; fifth band; green). The latter three bands were combined and subjected to further purification by SEC to provide the desired triple-decker type-a (yellowish green), type-b/c triple-decker (green), and the heteroleptic double-decker **(Por^{Tpd})Ce(Pc)** (green). Each of these components was subjected to further purification by chromatography [type-a triple decker [silica, CH_2Cl_2/hexanes (1:1)], type-b/c triple decker (silica gel, CH_2Cl_2), and **(Por^{Tpd})Ce(Pc)** double decker (silica gel, CH_2Cl_2)]. Following chromatography, each of these products was subjected to further purification by washing with methanol and hexanes as described for the type-a europium triple decker. The characterization data for each triple decker/double decker are given below.

(Por^{Tpd})Ce(Pc)Ce(Por^{Tpd}). Yield (11.4 mg, 6.4%); ^{1}H NMR (−2.54)−(−1.9) (m, 8H), (−1.74)−(−1.2) (m, 8H), 1.08−1.24 (m, 18H), 1.26−1.40 (m, 12H), 2.18 (br, 8H), 3.10−3.56 (m, 24H), 3.92−4.10 (m, 12H), 4.26−4.44 (m, 6H), 7.08−7.24 (m, 8H), 10.10−10.62 ppm (m, 8H); LD-MS obsd 2369.0; ESI-MS obsd 2369.7288, calcd 2369.7443 [(M + H)$^+$; M = $C_{146}H_{112}Ce_2N_{16}$]; λ_{abs} (toluene) 362, 421, 484, 549, 609 nm.

(Pc)Ce(Por^{Tpd})Ce(Pc)/(Pc)Ce(Pc)Ce(Por^{Tpd}). Yield (13 mg, 4%); ^{1}H NMR (300 MHz) (−8.7)−(−7.4) (m, 8H), (−5.2)−(−3.7) (m, 8H), (−0.72)−(−0.52) (m, 9H), (−0.18)−(0.03) (m, 6H), 2.12−2.52 (m, 8H), 2.56−2.84 (m, 3H), 3.0−3.28 (m, 6H), 4.7−5.6 ppm (m, 32H); LD-MS obsd 2092.3; ESI-MS obsd 2093.5378, calcd 2093.5062 [$(M + H)^+$; M = $C_{121}H_{80}Ce_2N_{20}$]; λ_{abs} (toluene) 344, 406, 453, 504, 617, 645, 755 nm.

(Por^{Tpd})Ce(Pc). Yield (57 mg, 26%); ^{1}H NMR 2.57−2.73 (m, 15H), 5.1−5.28 (m, 6H), 5.74−5.90 (m, 3H), 6.20−6.42 (m, 4H), 6.92−7.12 (m, 4H), 7.12−7.24 (m, 4H), 7.44−7.64 (m, 4H), 8.23−8.36 (m, 16H), 9.20−9.29 ppm (m, 8H); LD-MS obsd 1441.3; ESI-MS obsd 1440.4406, calcd 1440.4431 ($C_{89}H_{64}CeN_{12}$); λ_{abs} (toluene) 334, 403, 471, 569, 620, 818 nm.

D. 2-[4-(4-Allylhepta-1,6-dien-4-yl)phenyl]-5,6-dicyanobenzimidazole (6). Following a reported procedure,[17] a solution of **4** (198 mg, 1.25 mmol) in NMP (2.5 mL) and a solution of **5** (300 mg, 1.25 mmol) in NMP (3.5 mL) were combined in a flask fitted with a Hickman still. The mixture was heated at 120 °C and stirred for 2 h. Then, $FeCl_3 \cdot 6H_2O$ (17 mg, 63 μmol) was added and oxygen was bubbled through the mixture with continued heating and stirring for 20 h. The cooled reaction mixture was diluted with ethyl acetate. The organic solution was washed with water and brine. The organic layer was dried (Na_2SO_4) and filtered. The filtrate was concentrated and chromatographed (silica, CH_2Cl_2/ethyl acetate gradient of 0−5%). Fractions containing the desired compound (strong blue fluorescence upon long-wave UV illumination) were concentrated to give a reddish solid, which was chromatographed over a short plug of alumina (CH_2Cl_2/ethyl acetate (9:1) → ethyl acetate) yielding a colorless solid (268 mg, 57%): mp 264−266 °C; ^{1}H NMR (acetone-d_6) 2.57 (d, J = 7.2 Hz, 6H), 4.88−5.11 (m, 6H), 5.56−5.69 (m, 3H), 7.61−7.68 (m, 2H), 8.21−8.31 (m, 4H), 12.89 ppm (br, 1H); ^{13}C NMR (acetone-d_6) 41.6, 44.0, 108.2, 116.9, 117.7, 126.4, 127.3, 128.0, 134.4, 150.2 ppm; FAB-MS obsd 379.1909, calcd 379.1923 ($C_{25}H_{22}N_4$).

E. 2-[4-(4-Allylhepta-1,6-dien-4-yl)phenyl]-5,6-dicyano-1-propylbenzimidazole (7). Following a reported procedure,[17] a sample of **6** (265 mg, 0.70 mmol) in NMP (2.5 mL) was heated to 120 °C and treated with DBU (105 μL, 0.70 mmol). After stirring for 2 min, iodopropane (105 μL, 0.70 mmol) was added, and the mixture was stirred for 15 min. A second dose of DBU (68 μL, 0.70 mmol) followed by iodopropane (68 μL, 0.70 mmol) was added, and 15 min later, a third identical round of DBU and iodopropane was added. After the mixture was stirred for 15 min, the reaction mixture was allowed to cool and was diluted with ethyl acetate. The organic solution was washed with water and brine. The organic layer was dried (Na_2SO_4) and filtered. The filtrate was concentrated and chromatographed (silica, CH_2Cl_2/ethyl acetate gradient of 0−5%). Some starting material was recovered (83 mg, 31%), and fractions containing the product were concentrated to give a colorless solid (183 mg, 62%): mp 132−134 °C; ^{1}H NMR 0.92 (t, J = 8.0 Hz, 3H), 1.82−1.93 (m, 2H), 2.52 (d, J = 8.8 Hz, 6H), 4.31 (t, J = 7.6 Hz, 2H), 4.98−5.09 (m, 6H), 5.50−5.63 (m, 3H), 7.53 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.88 (s, 1H), 8.19 ppm (s, 1H); ^{13}C NMR 11.4, 23.5, 41.9, 44.1, 47.3, 108.5, 109.0, 116.7, 116.8, 118.5, 126.1, 126.4, 127.9, 129.2, 134.0, 137.9, 145.4, 149.9, 159.4 ppm; Anal. Calcd for $C_{28}H_{28}N_4$: C, 79.97; H, 6.71; N, 13.32; Found: C, 79.93; H, 6.73; N, 13.35.

F. 2-[4-(4-Allylhepta-1,6-dien-4-yl)phenyl]-1-propylimidazo-[4,5-*f*]isoindole-5,7(1*H*,6*H*)-diimine (8). Following a reported procedure,[25] a sample of **7** (105 mg, 0.25 mmol) in anhydrous MeOH (4 mL) under an argon atmosphere was heated at 70 °C. When the mixture became homogeneous, NaOMe (6 μL of a 25 wt % solution in MeOH, 25 μmol) was added, the argon line was removed from the apparatus, and ammonia gas was bubbled through the mixture while the mixture refluxed for 3.5 h. During this time, additional MeOH (0.5 mL) was added at half-hour intervals to prevent the reaction mixture from evaporating to dryness. The reaction flask was allowed to cool to room temperature under an atmosphere of ammonia, and then the ammonia flow was stopped. The mixture was allowed to stand overnight under a slowly flowing stream of argon, whereupon most of the solvent evaporated, and a white powder formed in the vessel. The mixture was filtered. The filtered material was washed with anhydrous MeOH and dried in vacuo (53 mg, 48%): mp 230−232 °C (upon which the sample melted and turned deep green). The presence of tautomeric forms of the product resulted in incomplete accounting for the protons: ^{1}H NMR (THF-d_8) 0.88 (t, J = 7.2 Hz, 3H), 1.82−1.96 (m, 2H), 2.56 (d, J = 7.2 Hz, 6H), 4.38 (t, J = 7.6 Hz, 2H), 4.97−5.10 (m, 6H), 5.57−5.70 (m, 3H), 7.57 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.84−8.40 ppm (m, 4H); ^{13}C NMR (THF-d_8) 10.6, 23.2, 41.8, 43.7, 46.4, 117.3, 127.2, 129.1, 134.5, 147.8 ppm; IR (film): 3397, 3276, 3200, 2958, 2927, 1536, 1432, 1149, 1121, 1077, 915.2 cm^{-1}; Anal. Calcd for $C_{28}H_{31}N_5$: C, 76.85; H, 7.14; N, 16.00; Found: C, 76.63; H, 7.21; N, 16.09. Note: The title compound does not entirely precipitate from the cooled reaction mixture. The recovery is aided by gently concentrating the mixture under a stream of argon until only a small quantity of liquid remains. Once precipitated, **8** does not readily redissolve in dry methanol, but a more soluble yellow byproduct was observed that redissolved even in preparations wherein the reaction mixture had been concentrated fully to dryness. Analysis of this byproduct (obtained from the methanolic filtrate after separating the product) by ^{1}H NMR spectroscopy confirmed that it was not **8**, but its identity was not determined.

G. Tribenzo[*g*,*l*,*q*]-(2-[4-(4-Allylhepta-1,6-dien-4-yl)phenyl]-1-propylbenzimidazo[5,6-*b*])porphyrazine (H_2-3). A 20-mL reaction vial was charged with **8** (43 mg, 98 μmol), **9** (169 mg, 392 μmol, 4 equiv), DMAE (5 mL), and a magnetic stirring bar. The vial was capped and heated in an oil bath maintained at 100 °C. Periodically, a few-microliter aliquot of the reaction mixture was removed, diluted into THF, and analyzed by UV−vis spectroscopy. After 8 h, **9** was not observed in the UV−vis spectrum. The reaction was then cooled to room temperature and diluted with MeOH (15 mL) and allowed to stand overnight. The mixture was centrifuged, and the supernatant was removed. MeOH (20 mL) was added to the pellet, and the mixture was sonicated and centrifuged again. After a third MeOH treatment and centrifugation, the pellet was dried in vacuo. The solid residue was suspended in THF (250 mL), sonicated, and filtered through Celite. The filtrate was set aside. The Celite was then added to a Soxhlet thimble and extracted overnight with CH_2Cl_2. The CH_2Cl_2 and THF filtrates were combined and concentrated to dryness. The solid residue was redissolved in a minimum of THF and chromatographed over a column of Bio-Beads SX-3 in THF. The desired compound was recovered from the column as a dark blue-green band that was closely followed by a blue band (unsubstituted phthalocyanine) and a faint pink band (remaining **9**). The fractions containing the desired compound were concentrated and rechromatographed over Bio-Beads SX-3 in THF. The sample was then chromatographed (silica, CH_2Cl_2, 1% 2-propanol, 5% THF, 5% ethyl acetate). Fractions containing the desired compound were concentrated to give a blue solid (25 mg, 32%): IR (KBr pellet): 2918, 1638, 1610, 1518, 1426, 1330, 1115, 1001, 912, 740 cm^{-1}; ^{1}H NMR (THF-d_8) −3.56 (br, 2H), 1.16 (t, J = 8.0 Hz, 3H), 2.12−2.24 (m, 2H), 2.75 (d, J = 6.8 Hz, 6H), 4.53 (t, J = 8.0 Hz, 2H), 5.15−5.28 (m, 6H), 5.78−5.91 (m, 3H), 7.57−7.64 (m, 1H), 7.67−7.74 (m, 1H), 7.76−7.89 (m, 6H), 8.06−8.16 (m, 3H), 8.16−8.24 (m, 1H), 8.47−8.54 (m, 2H), 8.57 (br, 1H), 8.62−8.72 ppm (m, 3H); LD-MS obsd, 807.0;

FAB-MS obsd 807.3717, calcd 807.3672 [(M + H)$^+$; M = $C_{52}H_{42}N_{10}$]; λ_{abs} 336, 651, 669, 695 nm; λ_{em} 700, 714 nm; Φ_f = 0.56 (THF).

H. Li_2-3. A sample of Li ribbon (19 mg, 2.9 mmol) was added to pentanol (14.5 mL), and the resulting mixture was refluxed until the Li was fully consumed (overnight). The full consumption of Li metal was considered important to avoid exposure of the allyl groups to any trace of unreacted Li metal. The mixture was cooled to room temperature and filtered through a pipet that was plugged with glass fiber paper. The filtrate was not titrated but was assumed to be ~0.2 M. Next, a sample of **H_2-3** (25 mg, 31 μmol) was added to pentanol (9.0 mL) and the mixture was briefly refluxed to dissolve all solid. Then, the sample was cooled to room temperature and the lithium pentoxide solution (1.0 mL) was added. The vessel was protected from moisture and placed in an oil bath at 140 °C. As the mixture was refluxed, samples (~2 μL) were taken periodically, diluted into freshly dried THF (3 mL) and analyzed by UV−vis absorption spectroscopy to monitor the progress of the reaction. After 15 min from the start of refluxing, the absorption spectrum of the removed sample had altered from the spectrum of the starting pigment (vide supra) to a new species having a more narrow Q-band. The mixture was refluxed for a total of 90 min. The reaction mixture was cooled to room temperature and concentrated to dryness on a high-vacuum rotary evaporator. The residue was taken up in dry acetone and added to a thimble in a Soxhlet apparatus. The residue was extracted with dry acetone until no further color appeared from the thimble. The filtrate from the extraction was concentrated to dryness. The residue was dissolved in a minimum of dry acetone and decanted to a vial, taking care not to transfer any insoluble **H_2-3** that may have formed during the extraction. The dark blue solution was then concentrated to dryness to give the product as a blue solid (10 mg, 39%). Due to the sensitivity of the product to moisture, the title compound was directly used in subsequent synthesis without characterization. The solids left behind in the evaporation flask and in the Soxhlet thimble were combined to recover the starting material **H_2-3** (15 mg, 60% recovery): λ_{abs} 602, 663, 671 nm.

I. (Por)Ce(Pc^{Tpd})Ce(Por). Following a reported procedure,[14] a 250-mL Schlenk flask containing a magnetic stirring bar was introduced into an argon glovebox. Cerium iodide (51 mg, 98 μmol) was added. The flask was sealed with a septum and removed from the glovebox. The flask was connected to an argon source, and the septum was vented with a needle. The flask was placed in an ice bath, and bis(2-methoxy)ethyl ether (3.0 mL, freshly sparged with argon) was added followed by $LiN(SiMe_3)_2$ (312 μL of a 0.608 M solution freshly prepared in dry THF and sparged with argon). The mixture was stirred for 20 min, after which the flask was removed from the ice bath and stirring was continued while the mixture warmed to room temperature over 40 min. The mixture was then refluxed for 1 h by placing the flask in an oil bath at 170 °C. The flask was then removed from the oil bath long enough for refluxing to subside, briefly opened to allow the addition of **H_2-10** (16 mg, 24 μmol), and closed again and returned to the bath to reflux for 3 h. Then, the vessel was again allowed to cool and opened to remove a small sample for UV−vis analysis. The sample was confirmed as the cerium−porphyrin half-sandwich, whereupon **Li_2-3** (10 mg, 12 μmol) was added as a slurry in bis(2-methoxyethyl) ether (1.0 mL). The resulting mixture was refluxed for 10 h under argon. The mixture was allowed to cool to room temperature and then was concentrated on a high-vacuum rotary evaporator. The residue was triturated with MeOH, centrifuged, and the supernatant was discarded. The residue was chromatographed (silica, neat CH_2Cl_2, then a mixture of CH_2Cl_2, 1% ^{i}PrOH, 5% THF, and 5% ethyl acetate). The first band was collected and rechromatographed [silica, hexanes/CH_2Cl_2 (1:2)]. Fractions containing the product were concentrated to give a green-black solid (9.0 mg, 30%): IR (KBr pellet): 2918, 1638, 1610, 1518, 1451, 1404, 1328, 1182, 1070, 986, 797, 740, 722 cm^{-1}; ^{1}H NMR (−2.45)−(−1.30) (m, 20H), 0.75−0.85 (m, 3H), 1.13 (br, 24H), 1.73 (d, *J* = 7.2 Hz, 6H), 1.90−2.20 (m, 6H), 2.80−3.60 (m, 24H), 4.35−4.42 (m, 6H), 4.68−4.82 (m, 3H), 5.45−5.62 (m, 2H), 6.20−6.35 (m, 2H), 7.09 (br, 8H), 10.34 ppm (br, 8H); LD-MS obsd, 2420.70; calcd 2420.74 ($C_{148}H_{112}Ce_2N_{18}$); λ_{abs} 359, 419, 493, 549, 608 nm.

III. Monolayer Preparation and Characterization. A. Electrode Preparation. The electrochemical measurements on the monolayers were made using highly doped p-type Si(100) working microelectrodes (100 μm × 100 μm) prepared via photolithographic methods as described previously.[28] A microelectrode was used to ensure that the RC time constant of the electrochemical cell was sufficiently short so that the electron-transfer kinetics of the triple-decker monolayers could be measured accurately.

A bare Ag wire was used as the counter/reference electrode. The electrode was prepared by sonicating a section of 500-μm-diameter Ag wire in 7.0 M NH_4OH, rinsing it in deionized water and ethanol, and then sonicating it in CH_2Cl_2 containing 1.0 M *n*-Bu_4NPF_6. The Ag wire prepared in this manner was placed inside a 10-μL polypropylene pipet tip containing ~5 μL of the propylene carbonate/1.0 M *n*-Bu_4NPF_6 electrolyte solution and manipulated using a micropositioning device in a setup previously described.[28]

B. Monolayer Preparation. All of the monolayers were assembled on hydrogen-passivated Si(100) surfaces, prepared as described previously,[28] by using a high-temperature (400 °C), short-time (2 min) "baking" attachment procedure previously shown to give facile attachment of alkenyl functionalized porphyrins to Si(100) surfaces.[29] The surface coverage and conditions for achieving saturation coverage were determined electrochemically in a series of experiments wherein the concentration of the triple decker in the deposition solution (benzonitrile) was varied systematically. These experiments revealed that the surface coverage could be varied in a controlled fashion from the low 10^{-12} mol cm^{-2} to the high 10^{-11} mol cm^{-2} range (saturation coverage) by varying the triple-decker concentration from ~2 μM to ~2 mM.

The monolayers for the electrochemical experiments were prepared by dispensing a 2-μL drop of the porphyrin solution onto the surface of the microelectrode contained in a sparged VOC vial sealed under Ar. The monolayers prepared for the FTIR experiments utilized much larger platforms (~1 cm^2) and consequently required a larger drop size, ~50 μL. After deposition, the vial containing the Si substrate was heated on a hotplate at 400 °C for 2 min and then removed and purged with Ar until cooled to room temperature. Finally, the Si substrate was rinsed and sonicated five times with anhydrous CH_2Cl_2 and purged dry once again under Ar.

IV. Electrochemical Measurements. The electrochemical measurements on the triple deckers in solution were made in a standard three-electrode cell using Pt working and counter electrodes and a Ag/Ag$^+$ reference electrode. The solvent/electrolyte was CH_2Cl_2 containing 0.1 M Bu_4NPF_6. The electrochemical measurements on the triple-decker monolayers were performed in a two-electrode configuration using the fabricated Si(100) microelectrode and the Ag counter/reference electrode described above[28] and propylene carbonate containing 1.0 M Bu_4NPF_6 as the solvent/electrolyte. A two-electrode mode is used for the voltammetric studies of the monolayers both for convenience and because the time-resolved electrochemical experiments (vide infra) utilize this configuration. The RC time constant for this microelectrode/electrochemical cell, measured to be ~4 μs, is sufficiently short to preclude any significant interference with the measurement of the electron-transfer rates. The cyclic voltammograms were recorded using a Gamry Instruments PC4-FAS1 femtostat running PHE 200 Framework and Echem Analyst software. The surface coverage of the triple decker in the monolayer was determined by integration of the total charge in the first anodic wave and by using the geometric dimensions of the microelectrode. The standard electron-transfer rate constants, k^0, of the triple-decker monolayers were obtained using the same SWAV method previously used to obtain k^0 values for porphyrin monolayers on both Au and Si surfaces.[7,28,30,32] The rates of charge dissipation after disconnection from the applied potential, reported as charge-retention half-lives, $t_{1/2}$, were obtained using the OCPA method also used previously to obtain $t_{1/2}$ values for porphyrin monolayers on both Au and Si surfaces.[28,31,38]

V. FTIR Spectroscopy. The FTIR spectra of the triple deckers in both solid and monolayer forms were collected at room temperature with a spectral resolution of 4 cm^{-1}. The spectra of solid triple deckers were obtained in KBr pellets (∼1−2 wt % porphyrin). These spectra were collected in transmission mode using a room-temperature DTGS detector by averaging over 32 scans.

The IR spectra of the triple-decker monolayers were obtained using a Harrick Scientific horizontal reflection Ge attenuated total reflection accessory (GATR, 65° incidence angle). The Si substrates were placed in contact with the flat surface of a semispherical Ge crystal that serves as the optical element, and IR spectra were collected with p-polarized light using a liquid-nitrogen-cooled medium-bandwidth (600−4000 cm^{-1}) MCT detector and averaging over 256 scans. The spectra of the triple-decker monolayers were referenced against that of a hydrogen-terminated Si(100) surface previously subjected to the same deposition conditions as those used to obtain the monolayer but using only the neat deposition solvent. The Ge crystal was cleaned with neat 2-butanone before every experiment, and the GATR accessory was purged with dry N_2 during data acquisition.

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