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Synthesis of Thiol-Derivatized Europium Porphyrinic Triple-Decker Sandwich Complexes for Multibit Molecular Information Storage

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The storage of multiple bits of information at the molecular level requires molecules with a large number of distinct oxidation states. Lanthanide triple-decker sandwich molecules employing porphyrins and phthalocyanines afford four cationic states and are very attractive for molecular information storage applications. Five triple-decker building blocks have been prepared of the type (phthalocyanine)Eu(phthalocyanine)Eu(porphyrin), each bearing one iodo, one ethyne, or one iodo and one ethyne group attached to the porphyrin unit. Two triple-decker building blocks with different oxidation potentials were derivatized with an *S*-acetylthiophenyl unit for attachment to an electroactive surface. To explore the preparation of arrays comprised of triple deckers, which may lead to the storage of a larger number of bits, two types of dyads of triple deckers were prepared. An ethyne-linked dyad of triple deckers bearing one *S*-acetylthiophenyl unit was prepared via repetitive Sonogashira couplings, and a butadiyne-linked dyad was prepared via a modified Glaser coupling. The triple deckers were characterized by absorption spectroscopy, laser-desorption mass spectrometry, and ^{1}H NMR spectroscopy. The thiol-derivatized triple deckers form self-assembled monolayers (SAMs) on gold via in situ cleavage of the thiol protecting group. The SAM of each array is electrochemically robust and exhibits three well-resolved, reversible oxidation waves. These electrochemical characteristics indicate that these types of molecules are well suited for storing multiple bits of information.

Introduction

The storage of information at the molecular level may afford extraordinarily high memory densities. The key feature in our approach toward molecular-based information storage lies in the storage of data in distinct molecular oxidation states.[1−5] 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. A general approach toward molecular-based information storage employs thiol-derivatized molecules attached to a gold surface. However, the use of thiols on gold restricts the available oxidation states to an electrochemical window that extends to ∼+1.2 V (versus Ag/Ag$^+$). This limit is dictated by electrolyte-induced corrosion of the Au surface. The lower bound on the window is determined by the potential at which the thiol-attached molecules are reductively desorbed (in the range ∼−0.5 to −1 V, depending on the exact nature of the thiol).[6] Thus, any increase in the number of oxidation states of the molecules must occur within this range. While multicomponent architectures comprised of multiple ferrocenes and porphyrins[2−4] can be envisaged to span this range, we sought to pursue molecules with a richer complement of redox states, especially with oxidation states at low potential.

Over the past two decades, a variety of sandwich molecules comprised of porphyrinic molecules and lanthanide metals has been created.[7] Such sandwich molecules are very attractive candidates for building molecular-based information storage devices owing to their large number of redox states. For example, four cationic states are typically exhibited by porphyrinic triple-decker sandwich molecules.[8,9] (Four anionic states are also accessible, but we have emphasized utilizing cationic rather than anionic oxidation states due to the greater stability of cations under real-world conditions.) Furthermore, with appropriate ligands and metals, the first oxidation potential of such triple deckers lies at low potential compared with that of monomeric porphyrins or phthalocyanines.

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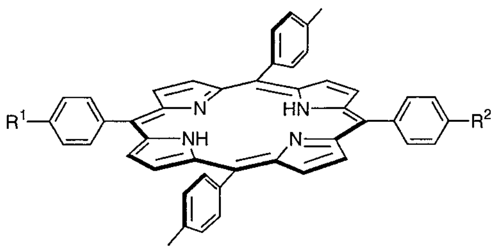
In this paper, we describe synthetic approaches that provide access to various triple-decker architectures for examination of multibit molecular information storage properties. A major objective of this work has been to investigate whether triple-decker building blocks can be prepared and joined into arrays analogous to those prepared from monomeric porphyrin building blocks.[10] We first prepared a set of triple-decker building blocks bearing trimethylsilylethyne and/or iodo groups. From these building blocks, two *S*-acetylthio-derivatized triple-decker molecules with different redox potentials have been prepared. As a first step in the investigation of the synthesis of arrays, two of the triple-decker building blocks were joined to afford an *S*-acetylthio-derivatized dyad of triple deckers. A butadiyne-linked dimer of triple deckers was prepared for solution electrochemical studies. All of the sandwich complexes prepared employ europium as the coordinated metal.

Results and Discussion

Strategy. To prepare triple-decker complexes for attachment to an electroactive surface, provisions must be made for incorporation of a thiol-derivatized linker. The joining of triple deckers to one another in arrays requires the attachment of synthetic handles to the triple deckers. In principle, the thiol linker and/or synthetic handles could be fastened to the porphyrin or the phthalocyanine unit in the triple deckers. Because the synthetic chemistry is much better developed for porphyrins than for phthalocyanines,[11] we have developed triple-decker building blocks that are constructed around suitably functionalized porphyrins. To avoid the possibility of any rotational isomers that might accrue from two functionalized porphyrins in one triple decker (as reported with two different porphyrins in a cerium double decker[12]), we have focused on preparing molecules comprised of one porphyrin and two phthalocyanines. Two isomers of such a triple decker are possible depending on whether the porphyrin is located in the middle or at the end of the sandwich. Given the greater yield of the triple decker with the porphyrin on the end of the sandwich (i.e., (Pc)M(Pc)M(Por)), we have pursued the synthesis of triple-decker building blocks of this general type.

The harsh nature of the reaction conditions for forming triple deckers precludes incorporation of a protected thiol unit or other sensitive groups in the porphyrin monomer prior to forming the triple decker. Thus, we have focused on preparing triple deckers bearing an iodo, ethyne, or both an iodo and an ethyne group. These synthetic handles provide the opportunity for elaboration of the triple-decker complexes into large molecular arrays or for attachment of thiol linkers via Pd-mediated coupling chemistry.

Chart 1



porphyrin	R^1	R^2
T-$PorH_2$	CH_3	CH_3
I-$PorH_2$	I	H
IE-$PorH_2$	TMS-ethynyl	I
E-$PorH_2$	TMS-ethynyl	CH_3

Triple-Decker Building Blocks. The general procedure for preparing mixed porphyrin-phthalocyanine sandwich complexes involves refluxing the porphyrin with excess $M(acac)_3{\cdot}nH_2O$ in 1,2,4-trichlorobenzene, affording the (porphyrin)M(acac) complex, followed by the addition of dilithium phthalocyanine (Li_2Pc) with continued reflux.[13] A mixture of double deckers and triple deckers is typically obtained, with the distribution of the products depending on reaction conditions, the nature of the metal, and the substituents on the macrocycles.[14-17]

We first sought to characterize the product distribution obtained with $Eu(acac)_3$ and the tetraarylporphyrins shown in Chart 1. Treatment of 5-(4-iodophenyl)-15-phenyl-10,20-di-*p*-tolylporphyrin (I-$PorH_2$)[18] with excess $Eu(acac)_3{\cdot}nH_2O$ in 1,2,4-trichlorobenzene afforded the corresponding (Por)Eu(acac). Treatment of the latter with Li_2Pc gave a mixture containing (I-Por)Eu(Pc)Eu(I-Por), (Pc)Eu(Pc)Eu(I-Por), and traces of (Pc)Eu(I-Por)Eu(Pc), (Pc)Eu(I-Por), and (Pc)Eu(Pc) (Scheme 1). The mixture could be partially separated by one silica gel column, affording bands comprised predominantly of (I-Por)Eu-(Pc)Eu(I-Por) contaminated with (Pc)Eu(I-Por) and starting porphyrin (I-$PorH_2$) [band 1], (Pc)Eu(I-Por) and starting porphyrin (I-$PorH_2$) [band 2], (Pc)Eu(I-Por)Eu-(Pc) [band 3], (Pc)Eu(Pc)Eu(I-Por) [band 4], and (Pc)Eu-(Pc) [top of column]. Further purification of band 1 by passage over one size exclusion chromatography (SEC) column afforded pure (I-Por)Eu(Pc)Eu(I-Por). A second silica column of band 4 afforded pure (Pc)Eu(Pc)Eu(I-Por). The triple deckers were characterized by absorption spectroscopy, laser-desorption mass spectrometry (LD-MS), and ^{1}H NMR spectroscopy. The isolated yields were as follows: (I-Por)Eu(Pc)Eu(I-Por) (17%), (Pc)Eu(I-Por)-Eu(Pc) (1%), and (Pc)Eu(Pc)Eu(I-Por) (14%). This product distribution resembles that of Jiang et al.,[17] though the isolated yield of (I-Por)Eu(Pc)Eu(I-Por) was substantially

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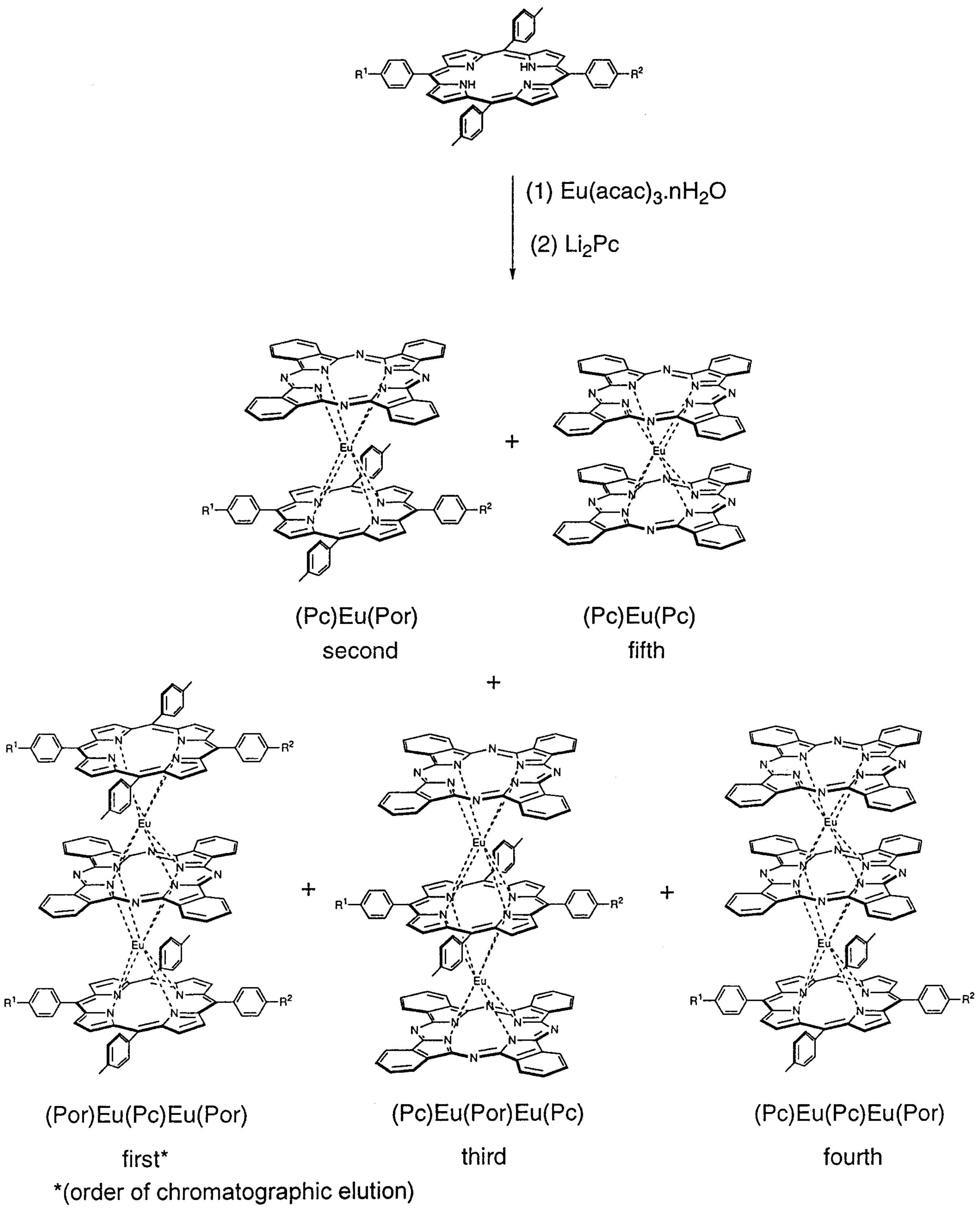
Scheme 1



lower than the 62% reported for the same kind of triple-decker complex. The triple-decker complex of the type (Pc)Eu(Por)Eu(Pc), though rarely isolated and obtained here in relatively low yield, is isomeric with (Pc)Eu(Pc)-Eu(Por). The two isomers can be readily distinguished by absorption and ^{1}H NMR spectroscopy (vide infra).

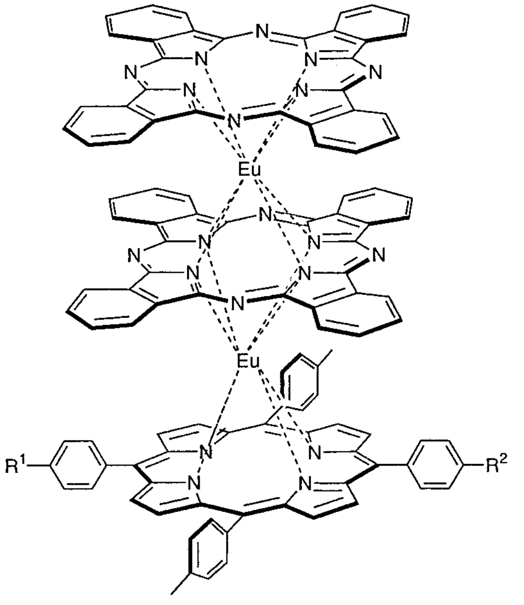
The same reaction conditions were employed with three other porphyrins, and analogous product distributions were obtained. The isolated yields of triple deckers from each reaction are summarized in Table 1. In each case, no decomposition of the synthetic handles (iodo, TMS-ethyne) was noticed. This approach afforded four

Table 1. Yields of Triple-Decker Building Blocks with Various Porphyrins[a]

	isolated yields (%)		
porphyrin	(Por)Eu(Pc)-Eu(Por)	(Pc)Eu(Por)-Eu(Pc)	(Pc)Eu(Pc)-Eu(Por)
T-PorH_2	23	3	10
I-PorH_2	17	1	14
E-PorH_2	9.5	0.5	9.1
IE-PorH_2	19	1.5	9.9

[a] Reactions were performed using a ratio of 1.5 mol of Pc component per 1 mol of porphyrin. Yields were calculated on the basis of the amount of porphyrin.

Chart 2

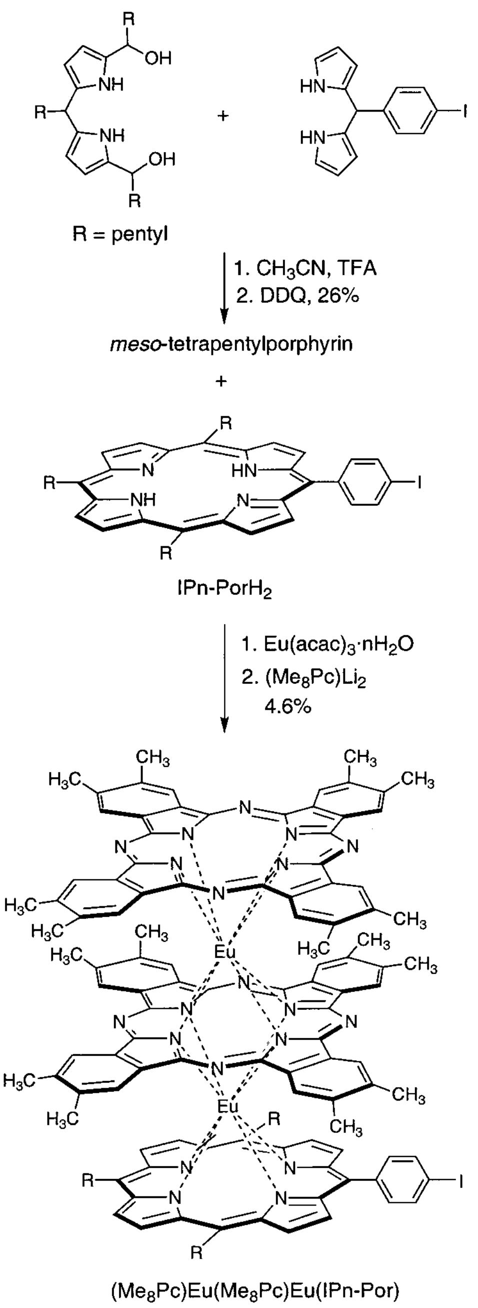


triple decker	R^1	R^2
(Pc)Eu(Pc)Eu(T-Por)	CH_3	CH_3
(Pc)Eu(Pc)Eu(I-Por)	I	H
(Pc)Eu(Pc)Eu(E-Por)	TMS-ethynyl	CH_3
(Pc)Eu(Pc)Eu(IE-Por)	TMS-ethynyl	I
(Pc)Eu(Pc)Eu(E′-Por)	ethynyl	CH_3

triple-decker building blocks of general structure (Pc)-Eu(Pc)Eu(Por) as shown in Chart 2. Deprotection of the TMS-ethynyl group of the triple decker (Pc)Eu(Pc)Eu(E-Por) afforded the corresponding ethynyl triple decker (Pc)Eu(Pc)Eu(E′-Por). The tetra-*p*-tolylporphyrin containing triple deckers have no synthetic handle but were prepared as a benchmark for ^1H NMR studies. The 4-fold symmetry of tetra-*p*-tolylporphyrin results in a much simpler ^1H NMR spectrum than observed with the porphyrins bearing one functional group (vide infra).

We also investigated the synthesis of a triple-decker building block with lower oxidation potentials. Lower oxidation potentials can be achieved by incorporation of electron-releasing groups on the phthalocyanine. Also, the replacement of porphyrin *meso*-aryl groups with *meso*-alkyl groups results in lower potentials due to the shorter interplanar distances in the sandwich molecules.[19] We sought to incorporate both features in a triple-decker complex. The requisite porphyrin was prepared by reaction of 5-(4-iodophenyl)dipyrromethane[20] and 1,9-bis(1-hydroxyhexyl)-5-pentyldipyrromethane[18] in the presence of TFA in acetonitrile followed by oxidation with DDQ (Scheme 2). Although this route with aryl-substituted substrates usually provides a single porphyrin devoid of other porphyrins due to acidolytic scrambling, dipyrromethane-dicarbinols with alkyl substituents condense with modest scrambling.[18] LD-MS analysis of the crude reaction mixture showed the presence of *meso*-tetrapentylporphyrin. Successive column chromatography afforded the desired porphyrin (IPn-PorH_2). Reaction of IPn-PorH_2 and $Eu(acac)_3 \cdot nH_2O$ followed by addition of the dilithium salt of octamethylphthalocyanine, $Li_2(Me_8$-

Scheme 2



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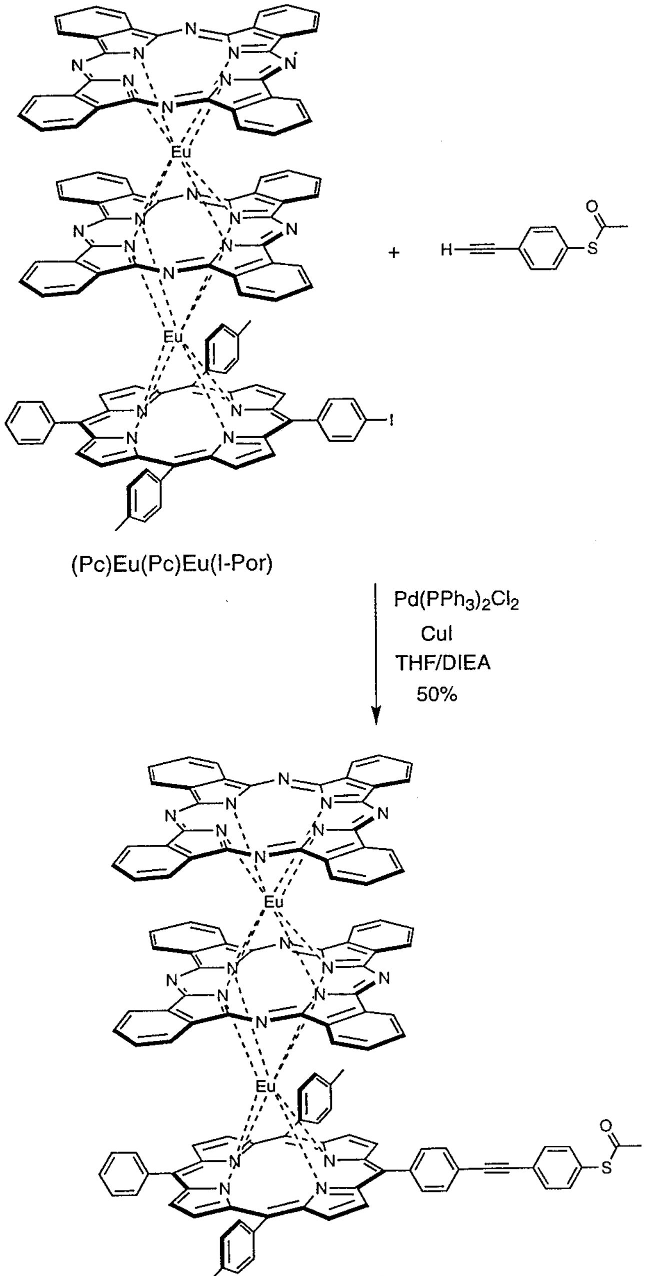
Pc),[21] gave the iodo-derivatized triple-decker complex $(Me_8Pc)Eu(Me_8Pc)Eu(IPn\text{-}Por)$ in 4.6% yield.

Synthesis of Thiol-Derivatized Triple-Decker Complexes. For applications in molecular information storage devices, the triple-decker complexes must be attached to an electroactive material such as a gold surface. The *S*-acetyl group is cleaved in situ on gold and is ideally suited for attachment of porphyrinic compounds.[22] We have explored two different approaches for introducing the *S*-acetylthio group into the triple-decker nucleus. During exploratory experiments, we found that the approach employing an iodo-substituted triple decker and 1-(*S*-acetylthio)-4-ethynylbenzene[23,24] was superior to the use of an ethynyl-substituted triple decker and 1-(*S*-acetylthio)-4-iodobenzene.[2] The superiority of the route employing the iodo-substituted triple decker stems from the side reactions that occur during Pd-mediated coupling.[25]

In our prior work with porphyrin building blocks, we developed mild conditions for Sonogashira coupling reactions ($Pd_2(dba)_3$, $AsPh_3$ or $P(o\text{-tol})_3$) that avoid use of copper cocatalysts.[26] Copper accelerates Pd-mediated coupling reactions but must be omitted in the synthesis of multiporphyrin arrays comprised of free base porphyrins in order to avoid adventitious metalation.[27] Such metalations are not possible with the lanthanide triple-decker complexes, and therefore, we examined the use of copper-accelerated Pd coupling conditions in these reactions.

The iodo-substituted triple decker (Pc)Eu(Pc)Eu(I-Por) and 1-(*S*-acetylthio)-4-ethynylbenzene were coupled using $Pd(PPh_3)_2Cl_2$, CuI, and DIEA in THF (Scheme 3). DIEA was used rather than the more common triethylamine because the *S*-acetylthio group undergoes cleavage in the presence of the latter but not the former.[23] No *S*-acetyl cleavage product was found in the reaction mixture. Purification via two silica columns gave the desired *S*-acetylthio-derivatized triple decker (TD1) in 50% yield.

Scheme 3



(Pc)Eu(Pc)Eu(I-Por)

TD1

The electron-rich iodo-substituted triple decker $(Me_8Pc)Eu(Me_8Pc)Eu(IPn\text{-}Por)$ was reacted with 1-(*S*-acetylthio)-4-ethynylbenzene under the same Pd-mediated coupling conditions. Purification of the reaction mixture afforded the *S*-acetylthio-derivatized triple-decker complex (TD2) in 10% yield (Scheme 4). A significant loss of material occurred during chromatography.

Dyads of Triple Deckers. The use of thiol-derivatized triple deckers for information storage provides the opportunity to access four cationic states, thereby storing two bits of information. To store additional information in one memory storage location, two different triple deckers can be employed where the four oxidation potentials of each are interleaved in a comblike manner, accessing eight cationic states and thereby storing three bits of information. Alternatively, two triple deckers can be incorporated in one molecular architecture. There are

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[25] An ethynyl-substituted triple decker of general type (Pc)Eu(Pc)Eu(Por) ($C_{122}H_{84}N_{20}Eu_2$, calcd average mass 2134) and 1-(*S*-acetylthio)-4-iodobenzene were coupled under the Pd-coupling conditions ($Pd_2(dba)_3$, $P(o\text{-tol})_3$) used for joining porphyrin building blocks.[26] LD-MS analysis of the crude reaction mixture revealed two dominant peaks (obsd 2179, 2287) corresponding to an unknown species and the desired product ($C_{130}H_{90}OSN_{20}Eu_2$, calcd average mass 2284), respectively. Column chromatography afforded the two separate species. ^1H NMR analysis of the unknown species revealed a sharp singlet (2.86 ppm, 3H) consistent with an acetyl moiety. We assign this species to an acetylated derivative of the ethynyl-substituted triple-decker starting material ($C_{124}H_{86}N_{20}OEu_2$, calcd average mass 2176). We ascribe this side reaction to the acetylation by 1-(*S*-acetylthio)-4-iodo-benzene (or product derived therefrom) of the ethynyl group attached to the triple-decker complex. Similarly, reaction of an ethynyl-substituted triple decker ($C_{139}H_{142}N_{20}Eu_2$, calcd average mass 2397) and 1-(*S*-acetylthio)-4-iodobenzene under copper-catalyzed Pd-coupling conditions ($Pd(PPh_3)_2Cl_2$, CuI) resulted in three major products, the acetyl-capped triple decker (LD-MS obsd 2440, calcd average mass 2439), the butadiyne-linked triple decker (LD-MS obsd 4788, calcd average mass 4791) derived from homo-coupling, and the desired *S*-acetyl-derivatized triple decker (LD-MS obsd 2549, calcd average mass 2547). The difficult separations posed by these side reactions can be avoided by use of an iodo-substituted triple decker and 1-(*S*-acetylthio)-4-ethynylbenzene. In this approach, *S*-acetyl transfer reactions affect only the starting 1-(*S*-acetylthio)-4-ethynylbenzene, not the triple decker. Small molecule byproducts are readily removed from the triple-decker product by size exclusion chromatography.

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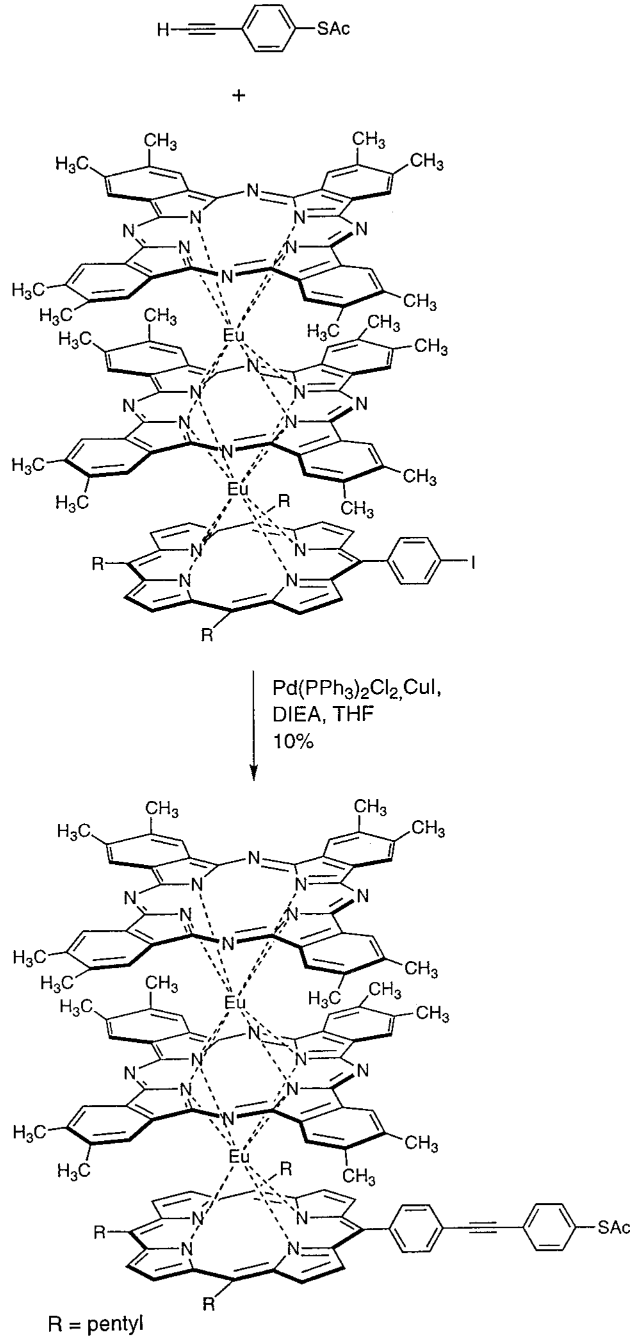
Scheme 4



TD2

at least two advantages of incorporating multiple redox-active groups in a molecular architecture. (1) The deposition of a homogeneous population of information storage molecules in a memory storage cell is not subject to partitioning effects as might occur with co-deposition on a surface of a mixture of molecules of different types. (2) The positioning of redox-active units in a vertical stack enables a higher surface concentration of redox-active molecules of a given type than would be possible upon co-deposition of a mixture of thiol-derivatized molecules each bearing one redox-active unit in a monolayer. To explore these advantages we have pursued the synthesis of a dyad of triple deckers. To our knowledge, dyads of triple deckers have heretofore not been synthesized.

To minimize handling of the *S*-acetylthio unit, the *S*-acetylthiophenyl unit was attached to the dyad of triple deckers in the last step of the synthesis (Scheme 5). In our first attempt, reaction of triple-deckers (Pc)Eu(Pc)-Eu(IE-Por) and (Pc)Eu(Pc)Eu(E′-Por) in the presence of $Pd(PPh_3)_2Cl_2$ and CuI afforded the desired ethyne-linked dyad (E-dyad-1) along with a butadiyne-linked dyad (not shown). The two dyads were easily separated from the other components of the reaction mixture by SEC; however, extensive chromatography was unsuccessful in separating the ethyne-linked dyad from the butadiyne-linked dyad. This mixture was carried through the next two reactions (TMS deprotection, coupling with 1-(*S*-acetylthio)-4-iodobenzene), whereupon the desired *S*-acetylthio-derivatized dyad of triple deckers (Dyad-1) was isolated in 3.8% overall yield. However, to avoid the self-coupling of (Pc)Eu(Pc)Eu(E′-Por), the alternative copper-free coupling conditions ($Pd_2(dba)_3$, P(*o*-tol)$_3$, no copper) were employed to prepare the ethyne-linked dyad (E-dyad-1). We previously prepared a series of multiporphyrin arrays under these copper-free Pd-mediated coupling conditions, and no self-coupling products were observed.[26,27] Thus, treatment of (Pc)Eu(Pc)Eu(IE-Por) with (Pc)Eu(Pc)Eu(E′-Por) under the copper-free Pd-mediated conditions afforded the desired ethyne-linked dyad (E-dyad-1) in 44% yield, and no butadiyne-linked dyad was detected. Treatment of E-dyad-1 with K_2CO_3 afforded E′-dyad-1 in 83% yield. The subsequent coupling ($Pd(PPh_3)_2Cl_2$, CuI) with 1-(*S*-acetylthio)-4-iodobenzene afforded a mixture containing the *S*-acetylthio-derivatized dyad (Dyad-1), the acetylation product of E′-dyad-1 as well as a trace of self-coupling products derived from E′-dyad-1.[25] One adsorption column (removal of the acetylation product) followed by one SEC column (removal of the butadiyne-linked self-coupling byproduct) afforded pure Dyad-1 in 22% yield.

Glaser Coupling To Yield a Butadiyne-Linked Dyad. We sought to prepare a butadiyne-linked dimer (Dyad-2) in order to (1) investigate the feasibility of performing a Glaser coupling using ethynyl triple deckers and (2) investigate the solution electrochemistry of a dimer of triple deckers. For the preparation of symmetrical diynes, a modified Eglinton-Glaser coupling (in the presence of CuCl/$CuCl_2$) has found increasing application.[28] However, treatment of (Pc)Eu(Pc)Eu(E′-Por) with CuCl/$CuCl_2$ in DMF in the absence or presence of an amine at room temperature only gave a trace of the product even after 24 h. The Pd(II)−Cu(I) catalyzed self-coupling of terminal alkynes in the presence of iodine has been found to give good to excellent yields with a broad range of terminal alkynes.[29] Thus, treatment of (Pc)Eu-(Pc)Eu(E′-Por) with $Pd(PPh_3)_2Cl_2$ and CuI in the presence of 0.5 molar equiv of iodine in toluene/*N*,*N*-diisopropylamine (5:1) gave the desired Dyad-2 in 89% yield (Scheme 6). The reaction was clean, and the product was easily separated by a single adsorption column followed by one SEC column.

Characterization of Triple-Decker Complexes. Each triple-decker complex was characterized by LD-MS, UV−vis, and ^{1}H NMR spectroscopy. LD-MS has proved particularly effective for identifying the composition of porphyrin-phthalocyanine sandwich complexes. In most cases, the triple deckers (Por)Eu(Pc)Eu(Por) and (Pc)Eu-(Por)Eu(Pc) each display the molecule ion peak and a fragment peak corresponding to [(Pc)Eu(Por)]$^+$. In con-

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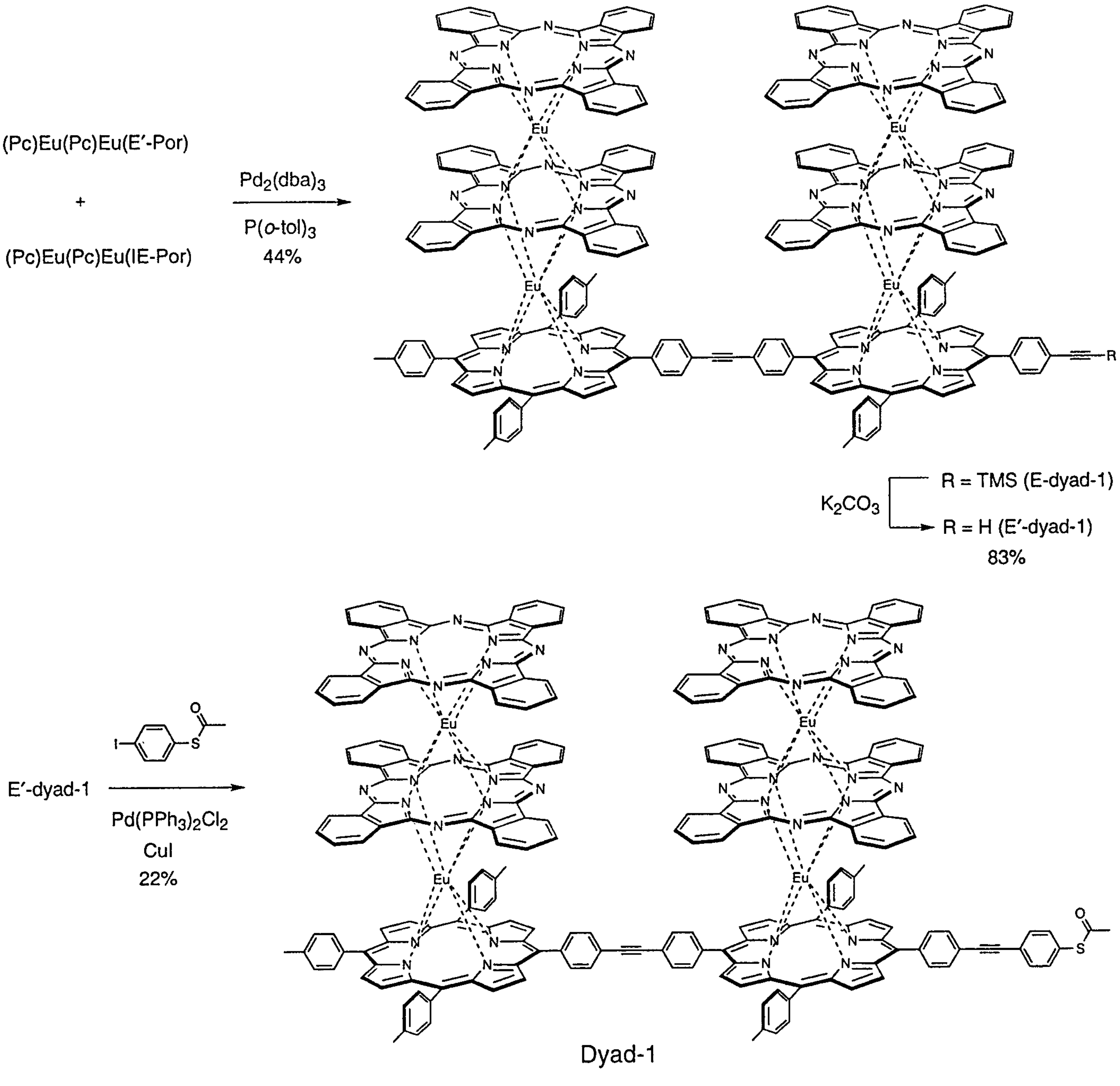
(29) Liu, Q.; Burton, D. J. *Tetrahedron Lett.* **1997**, *38*, 4371−4374.

Scheme 5

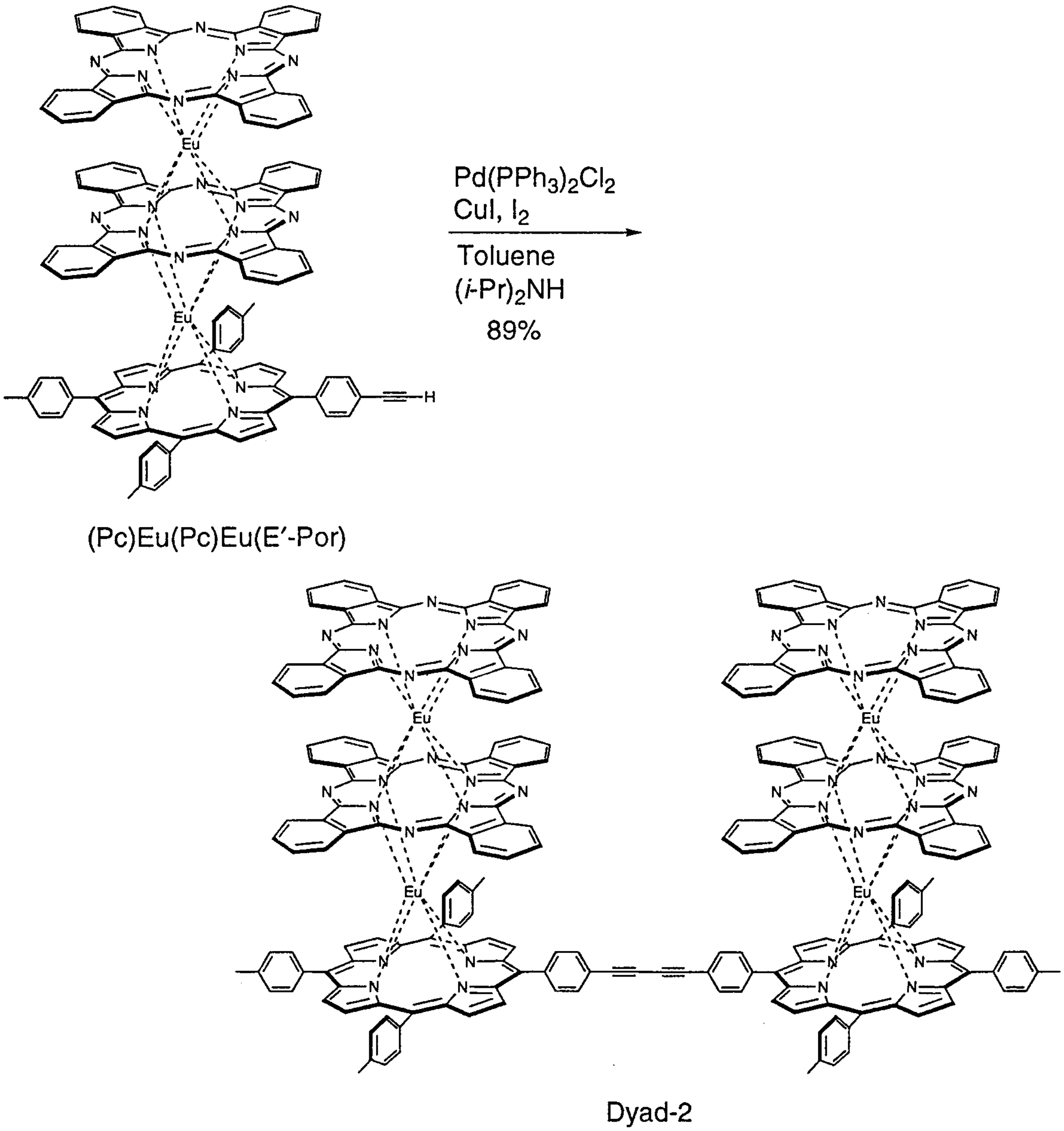


trast, the triple-decker complexes such as (Pc)Eu(Pc)Eu(Por) exhibit a molecule ion peak and two additional fragment peaks corresponding to [(Pc)Eu(Pc)]$^+$ and [Eu(Por)]$^+$. However, the triple decker (Me$_8$Pc)Eu(Me$_8$Pc)Eu(IPn-Por) gave only one major peak without clearly identifiable fragment peaks.

The UV–vis spectra of the triple-decker complexes of general structure (Por)Eu(Pc)Eu(Por) exhibit absorption at 341–354 nm and 415–420 nm, which are attributed to the phthalocyanine and porphyrin Soret bands, respectively.[9] The remaining absorption bands in the visible region are mainly attributed to the Q bands of the phthalocyanines. The isomers (Pc)Eu(Pc)Eu(Por) and (Pc)Eu(Por)Eu(Pc) are readily distinguished by UV–vis absorption spectroscopy. Both triple deckers exhibit less intense "porphyrin-type" bands due to the decrease in ratio of porphyrin/phthalocyanine compared with (Por)Eu(Pc)Eu(Por). The triple decker (Pc)M(Pc)M(Por) exhibits a diminished Soret band at 415–420 nm compared with the triple decker of the general type (Por)Eu(Pc)Eu(Por), while the triple decker (Pc)M(Por)M(Pc) exhibits a new broad band around 444 nm and no significant absorption between 415 and 420 nm. The absorption spectra of (Pc)Eu(Por)Eu(Pc) are in agreement with those reported for the same kind of cerium(III) triple-decker complexes.[16]

The ^{1}H NMR spectrum of (T-Por)Eu(Pc)Eu(T-Por) shows broad singlets at 12.75 and 10.64 ppm, which can be assigned to the α and β protons of the phthalocyanine. The doublets at 11.77, 8.92, 6.57, and 4.78 ppm are attributed to the phenyl protons. The presence of four signals for these protons reflects restricted rotation around the C(meso)–C(phenyl) bond. The singlet at 3.92 ppm is assigned to the porphyrin β-pyrrole protons, which are shifted upfield in comparison to the same signal in the spectrum of T-PorH$_2$. The presence of only one signal for the 16 β-pyrrole protons of the porphyrin and the 24 methyl protons is consistent with the symmetrical struc-

Scheme 6



ture of (T-Por)Eu(Pc)Eu(T-Por) (two outer porphyrins and one inner phthalocyanine). The spectral pattern of the triple decker (T-Por)Eu(Pc)Eu(T-Por) is very similar to that reported by Jiang et al.[17] for the triple-decker complex (TPP)Eu(Pc)Eu(TPP) derived from tetraphenylporphyrin (TPPH$_2$).

The ^{1}H NMR spectrum of the triple-decker complex (Pc)Eu(Pc)Eu(T-Por) shows four broad partially resolved resonances at 12.94, 11.04, 10.11, and 8.72 ppm with equal integration, attributed to the α and β protons of two nonequivalent phthalocyanines (inner and outer in the triple-decker sandwich). The doublets at 12.22, 9.07, 6.63, and 4.82 ppm are ascribed to the aromatic protons on the phenyl rings. The same pattern of these signals as described for (T-Por)Eu(Pc)Eu(T-Por) implies nonequivalent protons on the phenyl rings. These results are consistent with the triple-decker structure (T-Por)Eu(Pc)-Eu(Pc) (one outer and one inner phthalocyanine ligand).

In contrast, the ^{1}H NMR spectra of triple deckers of general structure (Pc)Eu(Por)Eu(Pc) revealed only two peaks at 9.59−9.71 and 8.05−8.22 (equal intensity) which are assigned to the α and β protons of the phthalocyanines, respectively, suggesting the symmetrical structure of the complexes. Also, unlike the isomeric (Pc)Eu(Pc)-Eu(Por) triple deckers, no peaks assigned to [(Pc)Eu(Pc)]$^+$ and [Eu(Por)]$^+$ were observed in the LD-MS spectra of the (Pc)Eu(Por)Eu(Pc) triple deckers. To our knowledge, few triple deckers of composition (Pc)M(Por)M(Pc) have been reported (and those are based on Ce(III)[16] or Eu-(III)[30]). In our studies reported herein, each triple-decker forming reaction gave rise to very small quantities of the triple decker (Pc)Eu(Por)Eu(Pc).

The triple-decker compounds derived from unsubstituted phthalocyanine were stable under the conditions described for preparation and routine handling, though those derived from the more electron-rich octamethylphthalocyanine were less stable. In general, the porphyrin-phthalocyanine sandwich complexes display satisfactory solubility in common organic solvents such as toluene, chloroform, and THF, a feature in sharp contrast

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(30) Arnold, D. P.; Jiang, J. *Chem. Lett.* **1999**, 483−484.

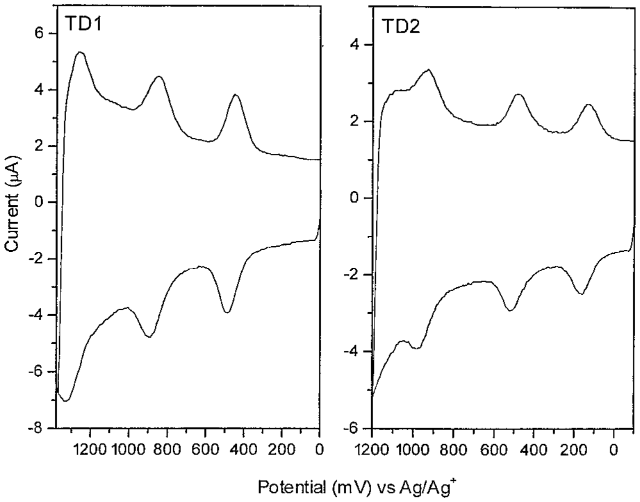

Figure 1. Fast-scan (100 V/s) voltammetry of TD1 (left panel) and TD2 (right panel).

with the poor solubility of phthalocyanines. The improved solubility is ascribed to the layered structure and nonplanar geometry of the end ligands in the triple deckers, which suppresses aggregation. Indeed, well-resolved ^{1}H NMR spectra were obtained of the triple deckers at concentrations in the few mM regime.

Electrochemical Studies. The electrochemical behavior of TD1, TD2, Dyad 1, and Dyad 2 was investigated in solution. Both TD1 and TD2 exhibit four reversible oxidation waves. The waves for TD1 are observed at $E_{1/2}(1) \sim 0.22$, $E_{1/2}(2) \sim 0.62$, $E_{1/2}(3) \sim 1.01$, and $E_{1/2}(4) \sim 1.29$ V. The waves for TD2 are observed at $E_{1/2}(1) \sim -0.05$, $E_{1/2}(2) \sim 0.33$, $E_{1/2}(3) \sim 0.79$, and $E_{1/2}(4) \sim 1.15$ V (all versus Ag/Ag$^+$; $E_{1/2}$ (FeCp$_2$/FeCp$_2^+$) = 0.19 V). Each of the four oxidation potentials of TD2 is shifted to a lower value compared with that of TD1 owing to the electron-releasing characteristics of the alkyl substituents on the rings of the former triple decker (vide infra). The values of the oxidation potentials of TD1 and TD2 are such that they interleave and are sufficiently separated that they could, in principle, be resolved from one another in a mixture of the two triple deckers, or in a dyad containing the two types. The two dyads (Dyad-1, Dyad-2) also exhibit four reversible oxidation waves. These waves occur at the same potential as those of TD1. This is expected because the constituents of the dyads have almost identical ring substituents as TD1. The observation of only four waves for the dyads also indicates that the electronic interactions between the constituent triple deckers in the dyads are very weak. This result is consistent with our earlier studies of porphyrin dimers containing similar linkers.[31]

The electrochemical behavior of the thiol-derivatized complexes TD1, TD2, and Dyad-1 was also investigated upon attachment to gold. All three arrays form self-assembled monolayers (SAMs) on gold via in situ cleavage of the *S*-acetylthio protecting group. The SAM of each array is electrochemically robust and exhibits three reversible, well-resolved oxidation waves. Representative fast-scan (100 V/s) cyclic voltammograms for TD1 and TD2 are shown in Figure 1. The waves for TD1 are observed at $E_{1/2}(1) \sim 0.47$, $E_{1/2}(2) \sim 0.88$, and $E_{1/2}(3) \sim 1.28$. The waves for TD2 are observed at $E_{1/2}(1) \sim 0.17$, $E_{1/2}(2) \sim 0.50$, and $E_{1/2}(3) \sim 0.93$. The SAM of Dyad-1 also exhibits three reversible, well-resolved oxidation waves (not shown). These waves occur at the same potentials as those of TD1. If there are differences in the potentials of the upper and lower triple deckers in Dyad-1, they are apparently too small to be resolved. Inspection of Figure 1 reveals that the differences in each successive oxidation potential for the SAMs of TD1 and TD2 are similar to those observed in solution. However, each wave for the SAM of both triple deckers is shifted ~0.15−0.2 V more positive relative to that observed in solution. This behavior is consistent with that observed for the SAMs of most of the other porphyrins we have investigated.[2−5] The positive shift in the oxidation potentials pushes the fourth wave for both triple deckers out of the useable window for the gold electrode under these conditions.

Conclusions

The cationic states of the lanthanide porphyrin-phthalocyanine triple-decker sandwich molecules are exceptionally attractive for molecular information storage applications. Triple-decker building blocks bearing ethyne, iodo, or iodo and ethyne groups can be prepared in a straightforward manner (though requiring considerable chromatography). Two *S*-acetylthio-derivatized triple deckers with different oxidation potentials were prepared for attachment to an electroactive surface. Two dyads of triple deckers have been prepared. An ethyne-linked dyad bearing an *S*-acetylthio unit was prepared for surface attachment, and a butadiyne-linked dyad was prepared for studies of solution electrochemistry. These syntheses demonstrate the successful use of the Sonogashira and Glaser coupling reactions with triple-decker building blocks. The electrochemical studies of the triple deckers indicate that multiple interleaved redox states can be achieved that afford access to molecules for multibit information storage. The synthetic chemistry described herein now makes possible a comparison of the information storage properties (writing/reading rates, charge retention) of a mixture of monomeric triple-deckers versus a homogeneous population of triple-decker arrays. The ability to work with triple deckers as building blocks augurs well for the attachment of a wide variety of linkers[2] and other redox-active moieties[3,4] in tailoring molecular arrays for desired multibit information storage properties.

Experimental Section

General Methods. Sources of reagents, solvents, and chromatographic media are described in the first paper of this series.[2] All ^{1}H NMR spectra were collected in CDCl$_3$ (300 MHz) unless noted otherwise. Absorption spectra were collected in toluene unless noted otherwise. Porphyrin−phthalocyanine sandwich complexes were analyzed by laser desorption mass spectrometry (LD-MS) and high-resolution fast atom bombardment mass spectrometry (FAB-MS). LD-MS analysis was done either without a matrix[32] or with the matrix POPOP.[33] Dilithium phthalocyanine (Aldrich, dye content ~70%), Eu(acac)$_3$·nH$_2$O (Alfa Aesar), and Pd(PPh$_3$)$_2$Cl$_2$ (Aldrich) were

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used as received. A rational synthetic method afforded 5-(4-iodophenyl)-15-phenyl-10,20-di-*p*-tolylporphyrin (I-PorH_2),[18] 5-(4-iodophenyl)-15-[4-[2-(trimethylsilyl)ethynyl]phenyl]-10,-20-di-*p*-tolylporphyrin (IE-PorH_2),[18] and 5-[4-[2-(trimethylsilyl)ethynyl]phenyl]-10,15,20-tri-*p*-tolylporphyrin (E-PorH_2). Preparative-scale size exclusion chromatography (SEC) was performed using BioRad Bio-beads SX-1 in a column (4.8 × 60 cm) with THF or toluene and eluted with gravity flow. Following purification, the SEC column was washed with two volume equivalents of solvent. Analytical scale SEC was performed with a 1000 Å column (5 μL, styrene-divinylbenzene copolymer) with THF as eluent (0.8 mL/min).[26]

5-[4-[2-(Trimethylsilyl)ethynyl]phenyl]-10,15,20-tri-*p*-tolylporphyrin (E-PorH_2). Following a standard procedure,[18,34] a solution of 5-(*p*-tolyl)dipyrromethane[20] (274 mg, 1.16 mmol) and the dicarbinol derived from 1,9-bis(*p*-toluoyl)-5-[4-(2-(trimethylsilyl)ethynyl)phenyl]dipyrromethane[34] (640 mg, 1.16 mmol) in CH_3CN at room temperature was treated with TFA (1.08 mL, 13.7 mmol) and then stirred for 5 min. Then DDQ (0.78 g, 3.4 mmol) was added, and the reaction mixture was stirred for 1 h. After passage of the crude reaction mixture over an alumina pad (CH_2Cl_2), column chromatography (silica, hexanes/CH_2Cl_2, 1:1) gave a purple solid (193 mg, 22%): ^{1}H NMR δ −2.80 (brs, 2H), 0.35 (s, 9H), 2.70 (s, 9H), 7.56 (d, J = 8.1 Hz, 6H), 7.87 (d, J = 8.1 Hz, 2H), 8.10 (d, J = 8.1 Hz, 6H), 8.17 (d, J = 8.1 Hz, 2H), 8.78−8.87 (m, 8H); LD-MS obsd 754.1; FAB-MS obsd 752.3361, calcd exact mass 752.3335 ($C_{52}H_{44}N_4Si$); λ_{abs} (CH_2Cl_2) 420, 516, 552, 593, 657 nm.

Exemplary Procedure for Preparing Triple Deckers, Given for (Pc)Eu(Pc)Eu(E-Por). A mixture of 5-[4-[2-(trimethylsilyl)ethynyl]phenyl]-10,15,20-tri-*p*-tolylporphyrin (140 mg, 0.19 mmol) and Eu(acac)$_3$·nH_2O (280 mg, 0.57 mmol) in 1,2,4-trichlorobenzene (35 mL) was heated to reflux and stirred under argon for 4 h. The resulting cherry-red solution was cooled to room temperature, and then Li_2Pc (220 mg) was added. The mixture was refluxed for an additional 5 h, and then the solvent was removed. The residue was dissolved in $CHCl_3$ and loaded onto a silica gel column packed with the same solvent. Elution with $CHCl_3$ afforded four bands. The first band (olive-brown) contained mainly (E-Por)Eu(Pc)Eu(E-Por) and unreacted porphyrin starting material and a small amount of the double-decker complex (Pc)Eu(E-Por). The second band (red) contained mainly porphyrin starting material and traces of double-decker complex (Pc)Eu(E-Por). The third band (black) contained triple-decker complex (Pc)Eu(E-Por)Eu(Pc). The last band (green) contained triple-decker complex (Pc)Eu(Pc)Eu(E-Por) and a small amount of the double-decker complex (Pc)Eu(Pc). A larger amount of the (Pc)Eu(Pc) remained near the top of the column.

The first band collected was redissolved in THF and loaded onto an SEC column. Elution with THF afforded (E-Por)Eu(Pc)Eu(E-Por) as the first band (greenish-brown), which after removal of the solvent and washing with methanol afforded a greenish-black solid (21 mg, 9.5%): ^{1}H NMR δ 0.64 (s, 18H), 2.99 (s, 18H), 3.86−3.96 (m, 16H), 4.77−4.89 (m, 8H), 6.58 (brs, 6H), 6.92 (m, 2H), 8.97 (brs, 6H), 9.35 (brs, 2H), 10.65 (brs, 8H), 11.90−12.08 (m, 8H), 12.75 (brs, 8H); LD-MS obsd 2321.9; FAB-MS obsd 2318.64, calcd exact mass 2318.63 ($C_{136}H_{100}N_{16}Si_2Eu_2$); λ_{abs} 355, 420, 491, 606, 657 nm.

The third band collected was also redissolved in THF and loaded onto an SEC column. Elution with THF afforded (Pc)Eu(E-Por)Eu(Pc) as the second band (black), which after removal of the solvent and washing with methanol afforded a black solid (2 mg, 0.5%): ^{1}H NMR δ 1.10 (s, 9H), 4.17 (s, 9H), 8.11 (brs, 16H), 9.62 (brs, 16H), 9.92 (m, 7H), 10.26 (m, 2H), 11.92−11.99 (m, 8H), 13.95−14.50 (m, 7H); LD-MS obsd 2083.7; FAB-MS obsd 2080.46, calcd exact mass 2080.46 ($C_{116}H_{74}N_{20}SiEu_2$); λ_{abs} 341, 444, 517, 628, 656, 796 nm.

The last band (green) collected was redissolved in toluene and loaded onto a short silica gel column packed with the same solvent. Elution with toluene afforded the first band (greenish-blue) containing the title compound, which after removal of the solvent and washing with methanol afforded a green solid (36 mg, 9.1%): ^{1}H NMR δ 0.69 (s, 9H), 3.00 (m, 9H), 3.15 (m, 8H), 4.83 (d, J = 7.2 Hz, 2H), 4.89 (d, J = 7.2 Hz, 1H), 5.03 (d, J = 7.2 Hz, 1H), 6.56 (t, J = 7.2 Hz, 3H), 6.96 (d, J = 7.2 Hz, 1H), 8.74 (brs, 8H), 9.11 (m, 3H), 9.53−9.55 (m, 1H), 10.13 (brs, 8H), 11.06 (brs, 8H), 12.30−12.42 (m, 3H), 12.62 (m, 1H), 12.95 (brs, 8H); LD-MS obsd 2083.2 (M^+), 1178.3 [M^+ − (E-Por)Eu], 903.1 [M^+ − (Pc)Eu(Pc)]; FAB-MS obsd 2080.45, calcd exact mass 2080.46 ($C_{116}H_{74}N_{20}SiEu_2$); λ_{abs} 342, 417, 522, 552, 618, 721 nm. (All yield calculations are based on the starting porphyrin.)

(Pc)Eu(Pc)Eu(T-Por). Following the general procedure, a small-scale reaction of *meso*-tetra-*p*-tolylporphyrin (35 mg, 0.052 mmol) afforded four bands (brown-red, red, black, green) upon chromatographic workup. The first band was redissolved in $CHCl_3$/THF and then chromatographed by SEC (THF), affording (T-Por)Eu(Pc)Eu(T-Por) as a greenish-brown solid (13 mg, 23%): ^{1}H NMR δ 2.98 (s, 24H), 3.92 (s, 16H), 4.78 (d, J = 6.6 Hz, 8H), 6.57 (d, J = 6.6 Hz, 8H), 8.92 (d, J = 6.6 Hz, 8H), 10.64 (s, 8H), 11.77 (d, J = 6.0 Hz, 8H), 12.75 (s, 8H); LD-MS obsd 2162.0, 1648.0, 1490.2, 1338.0, 823.6; FAB-MS obsd 2154.48, calcd exact mass 2154.58 ($C_{128}H_{88}N_{16}Eu_2$); λ_{abs} 356, 420, 490, 607 nm. The second band afforded (T-Por)Eu(Pc) as a brownish red solid (3 mg, 4%). LD-MS obsd 1338.1, calcd average mass 1333.3. The third band afforded (Pc)Eu(T-Por)Eu(Pc) as a black solid (3 mg, 3%). LD-MS obsd 2004.7, calcd average mass 1997.8. The fourth band was redissolved in toluene/$CHCl_3$ and chromatographed on silica (toluene), affording the title compound as a green solid (10 mg, 10%): ^{1}H NMR δ 3.06 (s, 12H), 3.19 (s, 8H), 4.92 (d, J = 6.6 Hz, 4H), 6.62 (d, J = 6.6 Hz, 4H), 8.74 (s, 8H), 9.15 (d, J = 5.1 Hz, 4H), 10.10 (s, 8H), 11.09 (s, 8H), 12.32 (s, 4H), 12.97 (s, 8H); LD-MS obsd 2001.2, 1644.6, 1178.5, 822.2; FAB-MS obsd 1998.49, calcd exact mass 1998.44 ($C_{112}H_{68}N_{20}Eu_2$); λ_{abs} 342, 414, 620, 718 nm.

(Pc)Eu(Pc)Eu(I-Por). Following the general procedure, reaction of 5-(4-iodophenyl)-15-phenyl-10,20-di-*p*-tolylporphyrin[18] (154 mg, 0.20 mmol) afforded four bands (olive-brown, red, black, green) upon chromatographic workup. The first band afforded (I-Por)Eu(Pc)Eu(I-Por) as a greenish-black solid (40 mg, 17%): ^{1}H NMR δ 2.96 (s, 12H), 3.91−3.95 (m, 16H), 4.63−4.86 (m, 8H), 6.56 (m, 4H), 6.76 (m, 2H), 7.09−7.11 (m, 2H), 8.10 (m, 2H), 8.88 (m, 4H), 9.13 (m, 2H), 9.49 (m, 2H), 10.65 (brs, 8H), 11.67 (brs, 4H), 11.91 (brs, 2H), 12.73 (brs, 8H); LD-MS obsd 2351.1; FAB-MS obsd 2350.33, calcd exact mass 2350.31 ($C_{124}H_{78}I_2N_{16}Eu_2$); λ_{abs} 355, 420, 491, 606, 657 nm. The third band afforded (Pc)Eu(I-Por)Eu(Pc) as a black solid (4 mg, 1%): ^{1}H NMR δ 4.13 (s, 6H), 8.08 (brs, 16H), 8.35 (s, 1H), 9.58 (brs, 16H), 9.91 (brs, 5H), 10.11 (m, 2H), 10.47 (m, 2H), 11.96 (brs, 8H), 13.90−14.09 (m, 7H); LD-MS obsd 2098.1; FAB-MS obsd 2096.30, calcd exact mass 2096.30 ($C_{110}H_{63}IN_{20}Eu_2$); λ_{abs} 343, 444, 517, 626, 652 nm. The fourth band afforded the title compound as a green solid (59 mg, 14%): ^{1}H NMR δ 2.98 (s, 6H), 3.18−3.22 (m, 8H), 4.72−4.92 (m, 4H), 6.55 (d, J = 7.2 Hz, 2H), 6.75 (t, J = 7.2 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 8.14 (m, 1H), 8.73 (brs, 8H), 9.08 (m, 2H), 9.29 (m, 1H), 9.68 (m, 1H), 10.11 (brs, 8H), 11.08 (brs, 8H), 12.19 (brs, 3H), 12.40 (m, 1H), 12.96 (brs, 8H); LD-MS obsd 2098.8 (M^+), 1177.8 [M^+ − (I-Por)Eu], 919.3 [M^+ − (Pc)Eu(Pc)]; FAB-MS obsd 2096.30, calcd exact mass 2096.30 ($C_{110}H_{63}IN_{20}Eu_2$); λ_{abs} 342, 414, 522, 617, 721 nm.

(Pc)Eu(Pc)Eu(IE-Por). Following the general procedure, reaction of 5-(4-iodophenyl)-15-[4-[2-(trimethylsilyl)ethynyl]phenyl]-10,20-di-*p*-tolylporphyrin[18] (261 mg, 0.30 mmol) yielded four bands (olive-brown, red, black, green) upon chromatographic workup. The first band afforded (IE-Por)Eu(Pc)Eu(IE-Por) as a greenish-black solid (72 mg, 19%): ^{1}H NMR δ 0.64 (s, 18H), 2.98 (s, 12H), 3.91 (m, 16H), 4.66−4.74 (m, 6H), 4.84−4.86 (m, 2H), 6.58 (d, J = 5.7 Hz, 4H), 6.92 (d, J = 5.7 Hz, 2H), 7.15 (m, 2H), 8.97 (d, J = 5.7 Hz, 4H), 9.36 (d, J = 5.1 Hz, 2H), 9.58 (d, J = 5.1 Hz, 2H), 10.67 (brs, 8H), 11.85 (m, 6H), 12.08 (m, 2H), 12.76 (brs, 8H); LD-MS obsd 2547.5; FAB-MS obsd 2542.41, calcd exact mass 2542.39 ($C_{134}H_{94}I_2Si_2N_{16}Eu_2$); λ_{abs} 356, 421, 493, 606 nm. The third band afforded

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(34) Cho, W.-S.; Kim, H.-J.; Littler, B. J.; Miller, M. A.; Lee, C.-H.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 7890−7901.

(Pc)Eu(IE-Por)Eu(Pc) as a black solid (10 mg, 1.5%): ^{1}H NMR δ 1.16 (s, 9H), 4.15 (s, 6H), 7.21 (s, 4H), 8.22 (brs, 16H), 9.71 (brs, 16H), 9.94 (brs, 4H), 10.26 (m, 2H), 10.46 (m, 2H), 11.97 (m, 6H), 13.94−14.14 (m, 6H); LD-MS obsd 2192.5; FAB-MS obsd 2192.35, calcd exact mass 2192.34 ($C_{115}H_{71}ISiN_{20}Eu_2$); λ_{abs} 341, 444, 517, 628, 656, 796 nm. The fourth band afforded the title compound as a green solid (65 mg, 9.9%): ^{1}H NMR δ 0.69 (s, 9H), 1.60 (s, 6H), 3.01−3.20 (m, 8H), 4.78 (m, 4H), 5.01 (m, 1H), 6.56 (m, 2H), 6.95 (m, 2H), 8.75 (brs, 8H), 9.12 (m, 2H), 9.57 (m, 1H), 9.76 (m, 1H), 10.12 (brs, 8H), 11.11 (brs, 8H), 12.29−12.42 (m, 2H), 12.66 (m, 1H), 12.98 (brs, 8H); LD-MS obsd 2195.1 (M$^+$), 1181.4 [M$^+$ − (IE-Por)Eu], 919.3 [M$^+$ − (Pc)-Eu(Pc)]; FAB-MS obsd 2192.34, calcd exact mass 2192.34 ($C_{115}H_{71}ISiN_{20}Eu_2$); λ_{abs} 342, 417, 522, 552, 618, 721 nm.

(Pc)Eu(Pc)Eu(E′-Por). A sample of (Pc)Eu(Pc)Eu(E-Por) (33 mg, 0.016 mmol) was dissolved in $CHCl_3$/CH_3OH (6 mL, 3:1). K_2CO_3 (20 mg, 0.14 mmol) was added, and the reaction mixture was stirred at room temperature under argon with occasional monitoring by ^{1}H NMR spectroscopy. Upon completion, $CHCl_3$ (30 mL) was added, and the resulting mixture was washed with 10% aqueous $NaHCO_3$ and H_2O, dried (Na_2SO_4), filtered, and concentrated. Column chromatography (silica, $CHCl_3$) afforded a black solid (31 mg, 97%): ^{1}H NMR δ 3.03 (m, 9H), 3.17−3.24 (m, 8H), 3.72 (s, 1H), 4.83 (m, 3H), 5.00 (d, J = 8.1 Hz, 1H), 6.56 (m, 3H), 6.96 (d, J = 7.2 Hz, 1H), 8.77 (brs, 8H), 9.13 (m, 3H), 9.53−9.55 (m, 1H), 10.18 (brs, 8H), 11.14 (brs, 8H), 12.22−12.32 (m, 3H), 12.50 (m, 1H), 13.03 (brs, 8H); LD-MS obsd 2008.6 (M$^+$), 1177.4 [M$^+$ − (E′-Por)-Eu], 831.0 [M$^+$ − (Pc)Eu(Pc)]; FAB-MS obsd 2008.43, calcd exact mass 2008.42 ($C_{113}H_{66}N_{20}Eu_2$); λ_{abs} 342, 416, 521, 618, 721 nm.

5-(4-Iodophenyl)-10,15,20-tri-*n*-pentylporphyrin. Following a standard procedure,[18,34] 5-(4-iodophenyl)dipyrromethane[20] (609 mg, 1.75 mmol) and a 1,9-bis(1-hydroxyhexyl)-5-pentyldipyrromethane[18] [prepared directly from 1,9-bis-(hexanoyl)-5-pentyldipyrromethane[18] (700 mg, 1.75 mmol) and used without purification] in CH_3CN was treated with TFA (1.62 mL, 21 mmol) for 4 min. Then DDQ (1.22 g, 5.25 mmol) was added, and the reaction mixture was stirred for 1 h. Column chromatography (silica, hexanes/CH_2Cl_2, 8:2 then 7:3) gave a purple solid (325 mg, 26%): ^{1}H NMR δ −2.69 (brs, 2H), 0.99 (t, J = 7.4 Hz, 6H), 1.03 (t, J = 7.1 Hz, 3H), 1.4−1.6 (m, 6H), 1.7−1.9 (m, 6H), 2.4−2.6 (m, 6H), 4.8−5.0 (m, 6H), 7.88 (AB/2, J = 8.1 Hz, 2H), 8.07 (AB/2, J = 8.1 Hz, 2H), 8.77 (d, J = 5.1 Hz, 2H), 9.36 (d, J = 4.2 Hz, 2H), 9.48 (AB, J = 4.8 Hz, 4H); LD-MS obsd 725.4; FAB-MS obsd 722.2854, calcd exact mass 722.2845 ($C_{41}H_{47}IN_4O$); λ_{abs} (CH_2Cl_2) 419, 517, 553, 591, 646 nm; λ_{em} (λ_{exc} 520 nm) 653, 718 nm.

(Me_8Pc)Eu(Me_8Pc)Eu(IPn-Por). Following the general procedure, a mixture of 5-(4-iodophenyl)-15,10,20-tri-*n*-pentylporphyrin (110 mg, 0.152 mmol) and Eu(acac)$_3$·nH$_2$O (235 mg, 0.47 mmol) in 1,2,4-trichlorobenzene (35 mL) was heated to reflux and stirred under argon for 4 h. The resulting cherry-red solution was cooled to room temperature, then Li$_2$(Me$_8$-Pc)[21] (440 mg, crude) was added. The mixture was refluxed for an additional 5 h, and then the volatile components were removed under vacuum. Chromatography of the residue (silica, $CHCl_3$) afforded four main bands (brown, containing (IPn-Por)-Eu(Me_8Pc)Eu(IPn-Por) and unreacted porphyrin starting material; light olive, containing (Me_8Pc)Eu(IPn-Por); olive, containing (Me_8Pc)Eu(IPn-Por)Eu(Me_8Pc), and dark green, containing (Me_8Pc)Eu(Me_8Pc)Eu(IPn-Por)). Chromatography of the first band (SEC, THF) afforded (IPn-Por)Eu(Me_8Pc)Eu-(IPn-Por) as the first band (olive-brown), which was finally purified on silica (toluene/hexanes, 30% hexanes to 0%) affording a brownish solid (20 mg, 11%): ^{1}H NMR δ −0.68 (brs, 4H), 0.59 (t, J = 6.6 Hz, 6H), 0.7−0.9 (m, 12H), 0.9−1.0 (m, 16H), 1.5−1.6 (m, 8H), 1.6−1.8 (m, 8H), 2.6−2.7 (m, 4H), 4.21 (s, 24H), 4.3−4.5 (m, 8H), 4.67 (m, 4H), 4.85 (d, J = 7.2 Hz 2H), 4.91 (s, 4H), 5.37 (d, J = 3.0 Hz, 4H), 6.24 (s, 4H), 7.11 (d, J = 7.5 Hz, 2H), 8.86 (d, J = 6.6 Hz, 2H), 9.1 (d, J = 7.5 Hz, 2H), 12.51 (s, 8H); LD-MS (POPOP as a matrix) obsd 2372.7, 2246.7; FAB-MS obsd 2370.65, calcd exact mass 2370.66, ($C_{122}H_{122}I_2N_{16}Eu_2$); λ_{abs} 365, 428, 502, 564, 623 nm. The second band was chromatographed (silica, toluene) affording (Me_8Pc)Eu(IPn-Por) as a brown solid (16 mg, 7.0%): LD-MS obsd 1499.24, 1442.0; FAB-MS obsd 1497.48, calcd exact mass 1497.47, ($C_{81}H_{77}IN_{12}Eu$); λ_{abs} 332, 407, 476 nm. The fourth band was chromatographed (silica, toluene) affording the main band (dark greenish-blue) containing the title compound and some unidentified impurities which were removed by a second column (silica, CH_2Cl_2/$CHCl_3$, 50% of CH_2Cl_2 to 0%), affording a dark green solid (16 mg, 4.6%). Each purification step led to the partial decomposition of product. The title compound gave the following data: ^{1}H NMR δ −0.22 (brs, 4H), 0.58 (t, J = 7.5 Hz, 3H), 0.6−2.5 (complicated pattern of multiplets), 3.8−3.9 (m, 4H), 3.99 (s, 24H), 4.1−4.3 (m, 4H), 4.35 (s, 24H), 4.71 (d, J = 7.5 Hz, 1H), 5.03 (s, 2H), 5.56 (s, 2H), 6.97 (d, J = 6.6 Hz, 1H), 7.5−7.7 (m, 1H), 8.49 (AB/2, J = 6.6 Hz, 1H), 8.56 (AB/2, J = 6.6 Hz, 1H), 10.02 (s, 8H), 12.80 (s, 8H); LD-MS obsd 2276.4, 2232.6, 2219.0, 2205.2, 2150.1; FAB-MS obsd 2274.66, calcd exact mass 2274.66 ($C_{121}H_{109}IN_{20}Eu_2$); λ_{abs} 351, 416, 536, 631, 746 nm.

***S*-Acetylthio-Derivatized Triple Decker (TD1).** Samples of (Pc)Eu(Pc)Eu(I-Por) (30 mg, 14 μmol), 1-(*S*-acetylthio)-4-ethynylbenzene[23,24] (20 mg, 0.11 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (1.5 mg, 2.1 μmol), and CuI (0.19 mg, 1.0 μmol) were added to a 25 mL Schlenk flask. The flask was evacuated and purged with argon three times. Then deaerated THF (5 mL) and deaerated DIEA (1 mL) were added by syringe. The flask was immersed in an oil bath at 30 °C and stirred under argon. The reaction was monitored by TLC (silica, toluene) and LD-MS. After 20 h, the solvent was removed under vacuum and the residue was dissolved in toluene/$CHCl_3$ (1:1) and loaded onto a silica gel column packed with the same solvent. Elution with toluene/$CHCl_3$ (1:1) afforded unreacted starting material and a deep green second band, which contained the desired product and also a minor amount of the starting material. The product thus obtained was further purified by a second column chromatography procedure (silica gel, toluene), affording a black solid (15 mg, 50%) after removal of the solvent and washing with methanol: ^{1}H NMR δ 2.62 (s, 3H), 2.99 (s, 6H), 3.20 (brs, 8H), 4.82 (d, J = 7.5 Hz, 2H), 4.96 (d, J = 6.6 Hz, 1H), 5.05 (d, J = 6.0 Hz, 1H), 6.56 (d, J = 7.5 Hz, 2H), 6.77 (m, 1H), 6.99 (m, 1H), 7.74 (d, J = 7.8 Hz, 2H), 8.05 (d, J = 8.1 Hz, 2H), 8.16 (t, J = 8.0 Hz, 1H), 8.73 (brs, 8H), 9.07 (m, 2H), 9.31 (m, 1H), 9.56 (m, 1H), 10.10 (brs, 8H), 11.08 (brs, 8H), 12.21 (m, 2H), 12.42 (m, 1H), 12.51 (m, 1H), 12.96 (brs, 8H); LD-MS obsd 2146.2 (M$^+$), 2104.2 (M$^+$ − CH_3CO), 1178.4 [M$^+$ − (I-Por)Eu], 968.2 [M$^+$ − (Pc)Eu(Pc)], 925.4 [M$^+$ − (Pc)Eu(Pc) − CH_3CO]; FAB-MS obsd 2144.42, calcd exact mass 2144.42 ($C_{120}H_{70}OSN_{20}Eu_2$); λ_{abs} 342, 416, 521, 618, 720 nm.

***S*-Acetylthio-Derivatized Triple Decker (TD2).** Samples of (Me_8Pc)Eu(Me_8Pc)Eu(IPn-Por) (30 mg, 13 μmol), 1-(*S*-acetylthio)-4-ethynylbenzene[23,24] (3 mg, 0.1 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (1.4 mg, 2.0 μmol), and CuI (0.18 mg, 0.95 μmol) were reacted in the presence of THF (4.9 mL) and DIEA (1.2 mL) at 30 °C using a Schlenk line. The reaction was monitored by TLC (silica, toluene/Et$_2$O, 50:1) and LD-MS. After 4 h, the reaction had stopped; thus, more 1-(*S*-acetylthio)-4-ethynylbenzene (6 mg, 0.3 mmol) was added. After 14 h, the solvent was removed under vacuum and the residue was dissolved in toluene and loaded onto a silica gel column packed with the same solvent. Elution with toluene and then toluene/Et$_2$O (50:1) did not afford total separation of the product from a small amount of impurities. The residue was redissolved in CH_2Cl_2 and chromatographed (silica, CH_2Cl_2 then CH_2Cl_2/$CHCl_3$) affording the desired ethyne-linked dyad (4 mg, 10%): ^{1}H NMR δ −0.25 (brs, 4H), 0.5−0.6 (m, 6H), 2.5−2.6 (complicated pattern of multiplets), 2.59 (s, 3H), 4.01 (s, 24H), 4.1−4.3 (m), 4.34 (s, 24H), 4.91 (d, J = 7.1 Hz, 1H), 4.98 (s, 2H), 5.51 (s, 2H), 6.75 (m, 1H), 7.65 (AB/2, J = 8.1 Hz, 2H), 7.94 (AB/2, J = 8.1 Hz, 2H), 8.3−8.4 (m, 1H), 8.7 (m, 1H), 9.90 (s, 8H), 12.70 (s, 8H); LD-MS 2331.1, 2288.45; FAB-MS obsd 2322.78, calcd exact mass 2322.78 ($C_{131}H_{111}N_{20}OSEu_2$); λ_{abs} 350, 418, 535, 585, 630, 750 nm.

E-dyad-1. Samples of (Pc)Eu(Pc)Eu(IE-Por) (35 mg, 16 μmol), (Pc)Eu(Pc)Eu(E′-Por) (32 mg, 16 μmol), Pd$_2$(dba)$_3$ (2.3 mg, 2.5 μmol), and P(*o*-tol)$_3$ (5.8 mg, 19 μmol) were reacted in the presence of toluene (5 mL) and triethylamine (1 mL) at

35 °C using a Schlenk line. The reaction was monitored by analytical SEC and LD-MS. After 15 h, the solvent was removed. The residue was dissolved in $CHCl_3$ and loaded onto a silica gel column. Elution with $CHCl_3$ afforded a main green band, which was concentrated to dryness, redissolved in toluene, and loaded onto a preparative SEC column packed with the same solvent. Elution with toluene afforded two well-separated green bands, of which the second band was collected. Removal of the solvent and washing with methanol afforded a black solid (28.5 mg, 44%): ^{1}H NMR δ 0.79 (s, 9H), 3.11, 3.16 (m, 15H), 3.36−3.61 (m, 16H), 5.00, 5.02 (m, 5H), 5.20 (m, 1H), 5.48 (m, 2H), 6.71, 6.74 (d, $J = 7.5$ Hz, 5H), 7.10 (m, 1H), 7.57 (m, 2H), 8.91 (brs, 16H), 9.25 (m, 6H), 9.68 (m, 1H), 10.09, 10.14 (m, 2H), 10.29 (brs, 16H), 11.30 (brs, 16H), 12.31−12.42 (m, 4H), 12.75, 12.85 (m, 2H), 13.04 (brs, 1H), 13.18 (brs, 16H); LD-MS obsd 4074.2; FAB-MS obsd 4072.72, calcd exact mass 4072.85 ($C_{228}H_{136}SiN_{40}Eu_4$); λ_{abs} 343, 425, 521, 617, 666, 720 nm.

E′-Dyad-1. A sample of E-dyad-1 (22 mg, 5.4 μmol) in $CHCl_3$/THF/CH_3OH (8 mL, 1:5:2) was treated with K_2CO_3 (20 mg, 0.14 mmol). The reaction mixture was stirred at room temperature under argon with occasional monitoring by ^{1}H NMR spectroscopy and LD-MS. Upon completion, $CHCl_3$ (30 mL) was added, and the resulting mixture was washed with 10% aqueous $NaHCO_3$ and H_2O, dried (Na_2SO_4), filtered, and concentrated. Column chromatography (silica, $CHCl_3$) afforded a black solid (18 mg, 83%): ^{1}H NMR δ 3.08−3.10 (m, 15H), 3.29−3.59 (m, 16H), 3.74 (s, 1H), 4.97 (m, 5H), 5.13 (m, 1H), 5.44 (m, 2H), 6.69 (d, $J = 7.2$ Hz, 5H), 7.21 (m, 1H), 7.54 (m, 2H), 8.86 (brs, 16H), 9.19 (brs, 6H), 9.58 (m, 1H), 10.18 (m, 2H), 10.25 (brs, 16H), 11.25 (brs, 16H), 12.23−12.36 (m, 4H), 12.52 (m, 1H), 12.82 (m, 2H) 13.14 (brs, 16H); LD-MS obsd 4008.3; FAB-MS obsd 4001.09, calcd exact mass 4000.81 ($C_{225}H_{128}N_{40}Eu_4$); λ_{abs} 343, 421, 523, 618, 667, 721 nm.

Dyad-1. Samples of E′-dyad-1 (15 mg, 3.8 μmol), 1-(*S*-acetylthio)-4-iodobenzene[2] (1.1 mg, 3.8 μmol), $Pd(PPh_3)_2Cl_2$ (0.4 mg, 0.6 μmol) and CuI (0.052 mg, 0.27 μmol) were reacted on a Schlenk line in the presence of toluene (3 mL) and deaerated DIEA (0.6 mL) at 30 °C under argon for 15 h with monitoring by TLC (silica, toluene) and LD-MS. (The tiny amounts of reagents were added by transferring 0.100 mL samples of the following stock solutions: $Pd(PPh_3)_2Cl_2$, 4.4 mg/1.1 mL toluene; CuI, 5.6 mg/10.7 mL DIEA.) The solvent was removed, and the residue was dissolved in toluene/Et_2O (50:1). Chromatography (silica, toluene/Et_2O 50:1) afforded the title compound as the first main band, which contained a trace of the butadiyne-linked dyad. Separation by SEC (toluene) afforded the title compound as the second band. Removal of the solvent and washing with methanol afforded a black solid (3.5 mg, 22%): ^{1}H NMR δ 2.66 (s, 3H), 3.08−3.11 (s, 15H), 3.27−3.60 (m, 16H), 4.95 (d, $J = 6.6$ Hz, 5H), 5.19 (m, 1H), 5.43 (m, 2H), 6.68 (d, $J = 7.2$ Hz, 5H), 7.10 (m, 1H), 7.53 (m, 2H), 7.77 (d, $J = 7.5$ Hz, 2H), 8.09 (d, $J = 7.5$ Hz, 2H), 8.86 (brs, 16H), 9.19 (d, $J = 5.7$ Hz, 6H), 9.66 (m, 1H), 10.05 (m, 2H), 10.25 (brs, 16H), 11.27 (brs, 16H), 12.32 (m, 4H), 12.62 (m, 1H), 12.81−12.87 (m, 2H), 13.15 (brs, 16H); LD-MS obsd 4156.4 (M^+), 4112.5 ($M^+ - CH_3CO$), 2981.8 ($M^+ -$ (Pc)Eu(Pc)); FAB-MS obsd 4150.55, calcd exact mass 4150.82 ($C_{233}H_{134}OSN_{40}Eu_4$); λ_{abs} 343, 418, 523, 618, 722 nm.

Dyad-2. To a mixture of (Pc)Eu(Pc)Eu(E′-Por) (18 mg, 9.0 μmol), $Pd(PPh_3)_2Cl_2$ (0.50 mg, 0.75 μmol), CuI (0.072 mg, 0.36 μmol) and I_2 (1.14 mg, 4.5 μmol) were added toluene (3 mL) and *N*,*N*-diisopropylamine (0.6 mL) and the resulting mixture was stirred at room temperature. (The tiny amounts of reagents were added by transferring 0.100 mL samples of the following stock solutions: $Pd(PPh_3)_2Cl_2$, 5.04 mg/1 mL toluene; CuI, 7.20 mg/10 mL *N*,*N*-diisopropylamine; I_2, 11.4 mg/1 mL toluene.) The reaction progressed slowly (monitored by analytical SEC), and after 4 h the same amount of $Pd(PPh_3)_2Cl_2$ and CuI were added. After stirring overnight the reaction was finished (product:starting material = 96:4 based on analytical SEC). The solvent was removed. Chromatography (silica, $CHCl_3$) removed all materials other than triple deckers. Subsequent purification by one SEC column (toluene) gave the desired compound as a black solid after washing with methanol (16 mg, 89%): ^{1}H NMR δ 3.04−3.07 (m, 30H), 3.27−3.41 (m, 16H), 4.90 (d, $J = 6.6$ Hz, 6H), 5.26 (m, 2H), 6.62 (d, $J = 7.5$ Hz, 6H), 7.30 (d, $J = 6.6$ Hz, 2H), 8.82 (brs, 16H), 9.13 (m, 6H), 9.85 (m, 2H), 10.21 (brs, 16H), 11.20 (brs, 16H), 12,21 (m, 6H), 12.61 (brs, 2H), 13.08 (brs, 16H); LD-MS obsd 4014.5; FAB-MS obsd 4014.68, calcd exact mass 4014.83 ($C_{226}H_{130}N_{40}Eu_4$); λ_{abs} 342, 421, 522, 618, 722 nm.

Electrochemistry. The solution and SAM electrochemical studies were conducted using the same instrumentation, techniques, and preparation strategies as described in Paper 1 of this series.[2] The solvent was CH_2Cl_2; tetrabutylammonium hexafluorophosphate (TBAH, 0.1 M) (Aldrich, recrystallized three times from methanol and dried under vacuum at 110 °C) served as supporting electrolyte. The potentials reported are vs Ag/Ag^+; $E_{1/2}(FeCp_2/FeCp_2^+) = 0.19$ V.

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Supporting Information Available: Absorption, LD-MS, and ^{1}H NMR spectra for each triple decker. This material is available free of charge via the Internet at http://pubs.acs.org.

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