Studies related to the design and synthesis of a molecular octal counter†

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An approach to the storage of multiple bits of information at the molecular level employs molecules with a large number of distinct oxidation states. Europium triple-decker sandwich molecules composed of porphyrins and phthalocyanines afford four cationic states and are very attractive for molecular information-storage applications. A larger number of states can be achieved by combinations of triple deckers that afford interleaved oxidation potentials. In order to identify suitable candidates for effective interleaving of oxidation potentials, a library of 19 new triple-decker complexes was prepared. Electron-donating groups have been attached to the porphyrin and/or phthalocyanine moieties in order to achieve oxidation states in the low potential regime. The triple deckers are of three different types: (Pc)Eu(Pc)Eu(Por), (Pc)Eu(Por)Eu(Pc), and (Por)Eu(Pc)Eu(Por). The solution electrochemistry of each member of the library was examined. These studies revealed suitable pairs of triple deckers that provide effective interleaving of oxidation potentials. Six triple deckers of type (Pc)Eu(Pc)Eu(Por) were derivatized with a thioacetyl or thiocyanate group on the porphyrin unit for attachment to an electroactive surface. Each of the S-(acetylthio)-derivatized triple deckers forms a self-assembled monolayer (SAM) on Au via in situ cleavage of the thiol protecting group. The SAM of each triple decker is electrochemically robust and exhibits four, well-resolved reversible oxidation waves. Upon disconnection from the source of applied potential, the triple-decker SAMs retain charge for tens to hundreds of seconds. The exact value of the charge-retention time depends on the specific porphyrin/phthalocyanine in the triple decker and the particular oxidation state of the molecules in the SAM (e.g., mono- vs. di- vs. tri- vs. tetracation). For all of the triple-decker SAMs, the charge-retention time monotonically increases as the oxidation state of the molecules in the SAM increases. Collectively, the studies suggest that the triple-decker complexes are excellent candidates for multibit molecular information storage elements.

Introduction

We recently embarked on a program aimed at constructing devices that use the properties of molecules to store information. Our general approach is to use the distinct oxidation states of redox-active molecules attached to an electroactive surface as the active storage medium. More specifically, we have demonstrated that self-assembled monolayers (SAMs) of oxidized, thiol-derivatized porphyrins on Au microelectrodes are capable of retaining charge for extended periods (tens of minutes) after disconnection from the source of applied potential.[1] This characteristic of porphyrin-based SAMs renders them attractive candidates for next-generation, molecular-based information storage media.

Another attractive feature of porphyrins as an information storage medium is that typically, at least two cationic oxidation states are readily accessible. This feature affords the possibility of storing multiple bits of information in a single molecule [where $\log_2$(number of states) = number of bits]. A molecule or molecular array with a larger number of accessible, easily distinguishable oxidation states would allow storage of even more information. Toward this goal, we have investigated a wide variety of redox-active molecules such as ferrocenes and

porphyrins as well as arrays comprised of multiple redox-active units.[1–6] Of these latter complexes, triple-decker phthalocyaninato and porphyrinato sandwich complexes of lanthanides and related metals have emerged as particularly attractive candidates for multibit information storage. The triple deckers generally exhibit four oxidation states in the range 0.0–1.4 V (vs. Ag/Ag+), corresponding to the formation of the mono-, di-, tri-, and tetracations.[7] The triple deckers also exhibit multiple anionic states. However, the cationic states are more attractive for information storage owing to their greater stability under real-world (i.e., oxidizing) conditions.

The fact that the triple deckers possess four readily accessible cationic oxidation states provides a counting range from one to four (where the neutral state is zero). The counting range could be extended to eight if two different triple deckers with interleaved and sufficiently well-separated oxidation states are used as the information storage element. Such a combination of triple deckers enables the storage of three bits of information and could potentially be used as an octal counter. In the most straightforward design, two triple deckers, each functionalized with a thiol linker, could be co-deposited in a single memory location. This construct requires that (1) the molecules exhibit similar partitioning onto the surface in the self-assembly process and (2) the SAM formed by co-deposition is sufficiently homogeneous that the interleaved oxidation waves remain well resolved. If these criteria are not met, an alternative approach to achieve a well-ordered monolayer with equimolar concentrations of the two different triple deckers would be to join the

two units in a covalent architecture bearing one or more thiol linkers. Regardless, the proper functioning of such an octal counter hinges in a large part on the design of the respective triple deckers such that the oxidation potentials are different and distinguishable.

We have recently developed a synthetic methodology for the preparation of triple-decker sandwich molecules of the general structure (Pc)Eu(Pc)Eu(Por) with a thiol-derivatized linker appended to the porphyrin unit.[6] The two thiol-derivatized triple deckers that we prepared (**TD1**, **TD2**) are shown in Chart 1. The thiol provides a site for attachment to Au. Our initial studies have shown that the thiol-derivatized triple deckers form SAMs on Au and exhibit robust, reversible electrochemical behavior.[6] While much is known about the electrochemical properties of monomeric metalloporphyrins, the literature on triple deckers is far less extensive and systematic.[8] Therefore, we elected to prepare a small systematic library of triple deckers of general formula (Pc)Eu(Pc)Eu(Por) and (Por)Eu(Pc)Eu(Por) with the immediate goal of understanding how substituents influence the oxidation potentials in these complexes. Our ultimate goal was to facilitate the rational design of an octal counter as well as other molecular devices built around triple-decker sandwich molecules for multibit information storage.

In this paper, we describe our initial studies aimed at developing an octal counter. We first describe the synthesis of the library of triple-decker complexes with electron-donating groups attached to the porphyrin and/or phthalocyanine units. Electron-donating groups have been employed in order to shift the oxidation states to lower potential. Next, we report the solution electrochemical characteristics of this family of triple-decker complexes. These studies revealed suitable combinations of triple deckers that provide effective interleaving of oxidation potentials. These insights prompted the synthesis of several thiol-derivatized triple deckers. We then proceed to describe the redox properties of SAMs formed from all of the thiol-derivatized triple deckers prepared to date. These studies include measurements of charge-retention (*i.e.*, the length of time the molecules remain oxidized after disconnection from the source of applied potential) in addition to conventional voltammetry. The charge-retention measurements are key because long charge-retention times are essential for a viable molecular-based memory storage element. We conclude with the results of co-deposition experiments aimed at constructing an octal counter.

Results and discussion

1. Triple-decker sandwich complexes for electrochemical studies in solution

Synthesis. The general procedure for the preparation of heteroleptic porphyrin-phthalocyanine sandwich complexes, developed by Weiss, is as follows.[9,10] A porphyrin is treated with excess Eu(acac)$_3$·nH$_2$O in refluxing 1,2,4-trichlorobenzene, affording the (porphyrin)Eu(acac) complex. Subsequent treatment with a dilithium phthalocyanine complex with continued reflux typically results in a mixture of unreacted starting materials, two double deckers, and three triple-deckers of composition (Por)Eu(Pc)Eu(Por), (Pc)Eu(Por)Eu(Pc), and (Pc)Eu(Pc)Eu(Por). The three triple-decker complexes are designated as types a, b and c, respectively (Scheme 1). The mixture is then separated chromatographically. Of the three types of triple deckers, the (Pc)Eu(Pc)Eu(Por) complex (type c) is most suitable for attachment of a thiol-derivatized linker
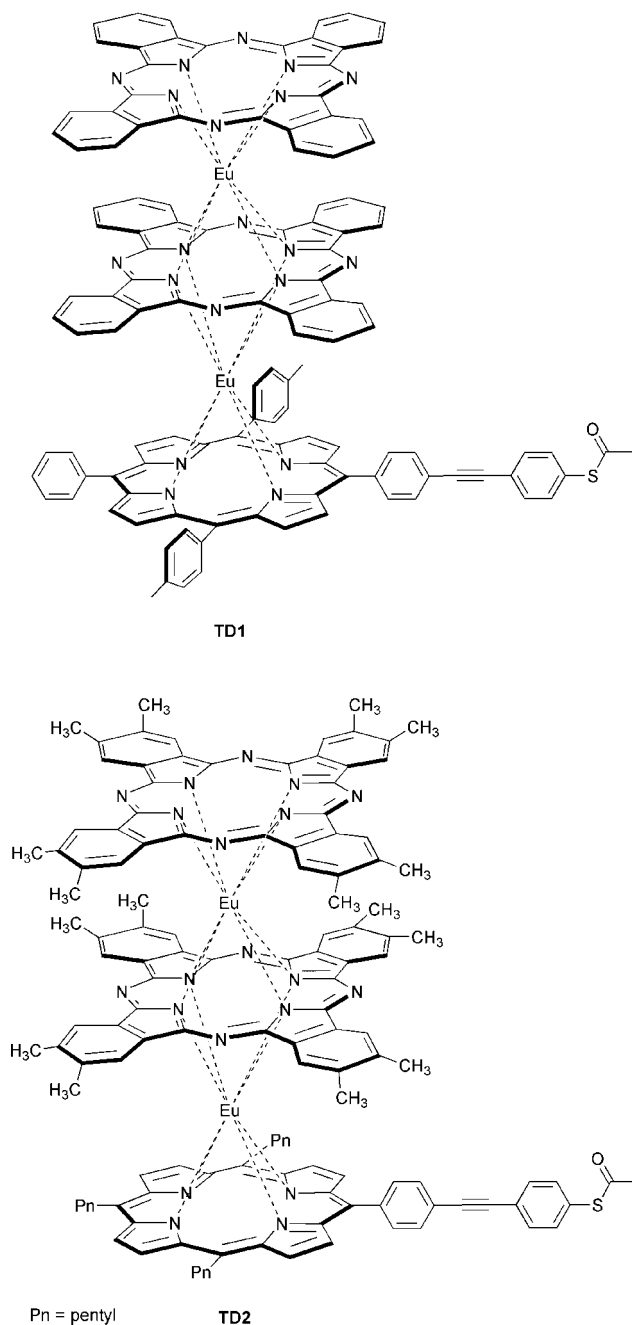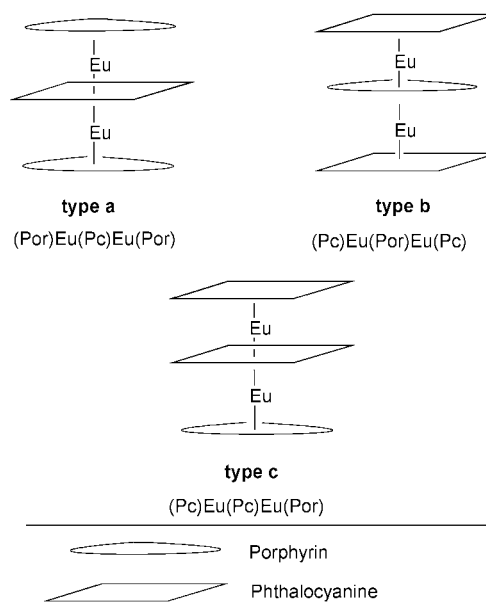

TD1

TD2

Pn = pentyl

Chart 1

type a	**type b**
(Por)Eu(Pc)Eu(Por)	(Pc)Eu(Por)Eu(Pc)

type c
(Pc)Eu(Pc)Eu(Por)

Porphyrin

Phthalocyanine

Scheme 1

(*vide infra*). We carried out the syntheses of the triple deckers generally using a 1:3:1.5 molar ratio of porphyrin:Eu(acac)$_3$·nH$_2$O:dilithium phthalocyanine,[7] with some exceptions (see Experimental section).

The porphyrins, dilithium phthalocyanines and dilithium naphthalocyanine used in the preparation of the library of triple deckers are shown in Chart 2.[11] The substituents to be examined include *n*-pentyl, phenyl, *p*-tolyl, or 4-*tert*-butylphenyl groups at the four *meso* positions of the porphyrin, ethyl groups at the eight β-positions of the porphyrin, and methyl, *n*-heptyl, *tert*-butyl, *n*-octyloxy, or *n*-butoxy groups at the perimeter of the phthalocyanine. Electron donating groups were chosen in order to obtain lower oxidation potentials. The lower oxidation potentials allow access to the lower portion of the electrochemical window afforded by the Au electrode. Note that dilithium tetra-*tert*-butylphthalocyanine [(t-Bu)$_4$PcLi$_2$] consisted of a mixture of regioisomers. The porphyrins were employed as the free base ligands, and the phthalocyanines were converted to the dilithium derivatives prior to reaction. We carried out the general reaction protocol with eleven combinations of porphyrin and phthalocyanine starting
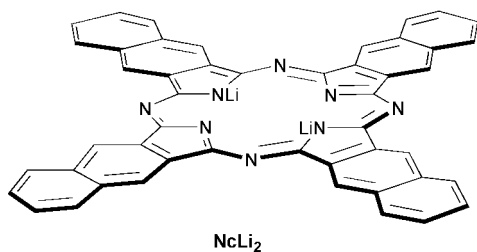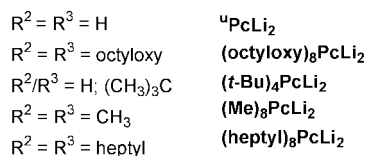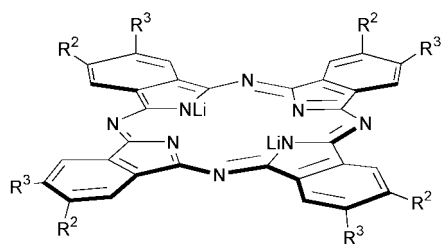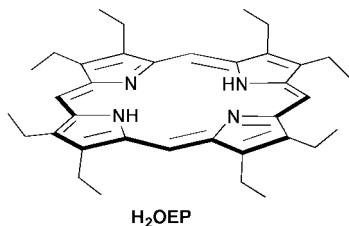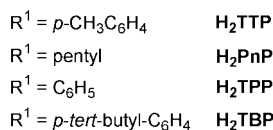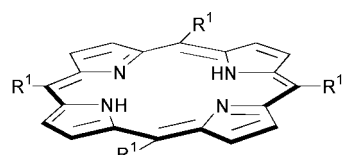
materials, which afforded the triple-decker complexes described in Table 1.

In each case, the crude reaction mixtures were purified by column chromatography on silica (CHCl$_3$). The first band contained the type-a triple-decker complex (Por)Eu(Pc)Eu(Por) and porphyrin monomer, which were easily separated by subsequent size-exclusion chromatography (SEC) with THF. The second and third bands contained triple-decker complexes of types b and c [(Pc)Eu(Por)Eu(Pc), (Pc)Eu(Pc)Eu(Por)], respectively, each of which required further silica column chromatography (toluene) for purification. In some cases (see Experimental section), additional chromatography was required to obtain pure triple deckers. In general, type-b complexes were formed in low yield and often were not isolated.

In a number of cases, slight differences from this general pattern were observed. (1) The triple-decker complex containing three tetra-*tert*-butylphthalocyanine ligands of general structure (Pc)Eu(Pc)Eu(Pc), **6d**, was isolated as the most polar triple-decker sandwich complex from the reaction of H$_2$PnP and (t-Bu)$_4$PcLi$_2$. (2) In the reaction of H$_2$OEP and (Me)$_8$PcLi$_2$, compound **9a** was isolated as the main product; b- and c-type triple-decker sandwich complexes were detected by laser-desorption mass spectrometry (LD-MS)[12] but were not isolated due to decomposition during chromatography. (3) The reaction of H$_2$OEP with (heptyl)$_8$PcLi$_2$ afforded only b- and c-type triple deckers; **10b** was isolated as the major product while only traces of **10c** were detected. (4) Some reactions proceeded very poorly. The reaction of H$_2$PnP and NcLi$_2$ resulted mainly in the recovery of starting material and a very small amount of the a-type triple-decker complex (**11a**). Reactions of dilithium 1,4,8,11,15,18,22,25-octabutoxyphthalocyanine with H$_2$TTP or H$_2$PnP led to the recovery of starting materials and a very complicated mixture of products, but triple-decker complexes were not present (as evidenced by LD-MS), presumably due to steric hindrance caused by the alkoxy substituents at the α-positions of the phthalocyanine. The yields of the triple-decker complexes isolated from each reaction are listed in Table 1. The preparation of complexes **1a–c** was described in our earlier paper.[6]

Each triple-decker complex was characterized by LD-MS, FAB-MS, UV-Vis spectroscopy and ^{1}H NMR spectroscopy. However, ^{1}H NMR spectroscopy was not particularly useful for characterizing complexes containing the tetra-*tert*-butylphthalocyanine ligand (**3a–c**, **6a,c,d**) due to the presence of phthalocyanine regioisomers. The purity of the complexes was confirmed by TLC and LD-MS analysis (in the absence of a matrix[12] unless otherwise noted). In the LD-MS spectra of **1a**, **1c**, **3a**, and **6a**, other peaks in addition to the molecule ion peak (M$^+$) were detected and could be assigned to fragmentation: (Por)Eu$^+$, (Por)Eu(Pc)$^+$ or M$^+$−[C$_4$H$_9$]. Type-a triple deckers were easily distinguished from types b and c by the significant differences in mass upon LD-MS analysis. Type-b and type-c compounds derived from the same starting materials are isomers; their structures were assigned based on UV-Vis and ^{1}H NMR spectroscopy. The spectra reported for (Pc)Eu(Pc)Eu(Por)[7,13] and for analogous Ce(III) triple-decker complexes[10] served as useful benchmarks for identifying the triple deckers prepared in this work.

Electrochemistry. Each member of the library of triple-decker sandwich complexes that was pure and available in sufficient quantity was examined electrochemically in solution. Selected electrochemical data are summarized in Table 2. Most of the triple deckers exhibit four oxidation waves in the range −0.2–1.4 V; compounds **3c** and **6d** exhibit three waves; compound **2c** exhibits only two waves. An upper bound of ~1.6 V was chosen for the solution studies because the Au electrodes used for the SAM studies limit the maximum potential to approximately this value (*vide infra*). The reduction

R^1 = *p*-CH$_3$C$_6$H$_4$ **H$_2$TTP**
R^1 = pentyl   **H$_2$PnP**
R^1 = C$_6$H$_5$ **H$_2$TPP**
R^1 = *p-tert*-butyl-C$_6$H$_4$ **H$_2$TBP**

H$_2$OEP

R^2 = R^3 = H ^{u}**PcLi$_2$**
R^2 = R^3 = octyloxy   **(octyloxy)$_8$PcLi$_2$**
R^2/R^3 = H; (CH$_3$)$_3$C   **(t-Bu)$_4$PcLi$_2$**
R^2 = R^3 = CH$_3$ **(Me)$_8$PcLi$_2$**
R^2 = R^3 = heptyl   **(heptyl)$_8$PcLi$_2$**

NcLi$_2$

Chart 2

Table 1 Yields of the triple-decker complexes[a]

Starting materials						Pc substituents	
Porphyrin	Phthalocyanine	Triple-decker complexes (% yield)[b]			Porphyrin substituents	R[2]	R[3]
H₂TTP	ᵘPcLi₂	**1a** (23)[c]	**1b** (3)[c]	**1c** (10)[c]	*meso*-4-CH₃C₆H₄	H	H
H₂TTP	(octyloxy)₈PcLi₂	**2a** (42)	**2b**	**2c** (11)	*meso*-4-CH₃C₆H₄	octyloxy	octyloxy
H₂TTP	(*t*-Bu)₄PcLi₂	**3a** (13)	**3b** (2.7)	**3c** (17)	*meso*-4-CH₃C₆H₄	R²/R³ = H, C(CH₃)₃	
H₂TBP	ᵘPcLi₂	**4a** (36)	**4b** (0.7)	**4c** (11)	*meso*-4-*t*-BuC₆H₄	H	H
H₂PnP	ᵘPcLi₂	**5a** (39)	**5b**	**5c** (30)	*meso*-pentyl	H	H
H₂PnP	(*t*-Bu)₄PcLi₂	**6a** (39)	**6b**	**6c** (11)	*meso*-pentyl	R²/R³ = H, C(CH₃)₃	
H₂PnP	(Me)₈PcLi₂	**7a** (8)	**7b**	**7c** (2)	*meso*-pentyl	CH₃	CH₃
H₂TPP	(Me)₈PcLi₂	**8a** (14)	**8b**	**8c** (8.9)	*meso*-C₆H₅	CH₃	CH₃
H₂OEP	(Me)₈PcLi₂	**9a** (20)[d]	**9b**	**9c**	β-ethyl	CH₃	CH₃
H₂OEP	(heptyl)₈PcLi₂	**10a**	**10b** (18)	**10c**	β-ethyl	heptyl	heptyl
H₂PnP	NcLi₂	**11a** (3)	**11b**	**11c**	*meso*-pentyl	annulation for Nc[e]	

[a]Type a complexes: (Por)Eu(Pc)Eu(Por). Type b complexes: (Pc)Eu(Por)Eu(Pc). Type c complexes: (Pc)Eu(Pc)Eu(Por). [b]All yield calculations are based on the amount of starting porphyrin. [c]Reference 6. [d]90% purity. [e]Naphthalocyanine.

process was not examined in detail given our preference for use of the cationic states for information storage. For those complexes that were examined, one or more reduction process was typically observed. The triple deckers with the highest potential for the first oxidation process (**1c**, **3a**, **3b**, **4b**) were comprised of tetraarylporphyrins and phthalocyanines with few electron-donating moieties. The lowest potential for the first oxidation process was observed with compound **9a**, which contains two octaethylporphyrin ligands and eight methyl groups on the phthalocyanine ligand.

The observation that electron-donating groups shift the oxidation potentials to lower potentials is consistent with the electronic effects of substituents on porphyrin electrochemistry.[14] The shifts in potential also stem in part from steric effects on inter-ring separation in the triple deckers.[15] These effects of substituents provide an entrée into interleaving oxidation potentials, as required for constructing an octal counter. In addition, low potential oxidation states afford greater stability

and also would provide for lower power consumption in a memory storage element based on these molecular materials.

2. Towards combinations of triple deckers for increased information storage

Strategy. In order to identify combinations of triple deckers that could be used in the design of an octal counter, we overlaid square wave voltammograms and inspected them visually for interleaved oxidation potentials. Some of the pairs that exhibited very good separations of potentials included the following: **6c/3a**; **1c/6a**; **3a/6a**; **1c/6c**; **1c/7c**; **4c/6c**; and **4c/7c**. Although a variety of combinations of triple deckers have suitable oxidation potentials for interleaving, only type-c triple deckers [(Pc)Eu(Pc)Eu(Por)] were chosen for thiol-derivatization. The rationale for choosing these complexes was as follows. (1) We elected to attach the functional group to a porphyrin unit because the synthetic chemistry for porphyrins is much better developed than for phthalocyanines.[16,17] Thus, the type-b and type-c triple deckers (which contain one porphyrin) are the most viable complexes. The type-a triple deckers (which contain two porphyrins) are less desirable because both porphyrins would be functionalized with no mechanism for controlling the relative orientation of the functional group on the two porphyrins. Indeed, rotational isomers have been reported for (Por)Ce(Por) double deckers.[18] (2) The type-c triple deckers were selected over the type-b complexes because the former complexes are generally obtained in much greater yield.

The next step was the choice of porphyrins for functionalization. Again owing to the more highly developed chemistry, *meso*-substituted porphyrins were chosen over β-substituted units.[16] Based on the solution redox potentials (Table 2), type-c triple deckers containing *meso*-alkyl or *meso*-aryl substituted porphyrins are the best candidates for obtaining mixed monolayers with distinguishable oxidation waves. Accordingly, a subset of these types of porphyrins was selected for functionalization.

The final step was the selection of linker and functional group for the porphyrin constituent. For four of the five triple deckers, we selected a *meso*-diarylethyne group; for the fifth triple decker we chose a *meso*-hexyl group in order to examine the effects of a more insulating linker. Finally, an *S*-acetylthio group was chosen as the preferred functional group for attachment to the linker. This group was chosen because (1) the *S*-acetylthio group is compatible with the chemistry used to synthesize both the porphyrins and triple deckers, and (2) the *S*-acetylthio group undergoes facile cleavage upon exposure to the Au surface.[1-6,19,20] A thiocyanate group was introduced on one linker in order to explore attachment to metals such as Pd or Pt in addition to Au.

Table 2 Half-wave potentials for the non-thiol-derivatized triple-decker complexes in solution[a]

Triple decker	Half-wave potential[b]						
	$E_{+3/+4}$	$E_{+2/+3}$	$E_{+1/+2}$	$E_{0/+1}$	$E_{0/-1}$	$E_{-1/-2}$	$E_{-2/-3}$
1a	+1.18	+0.93	+0.61	+0.19			
1c	+1.29	+1.01	+0.62	+0.23	−0.91	−1.37	−1.85
2a	+1.12	+0.91	+0.53	+0.19	−1.21	−1.68	
2c			+0.35	+0.06	−1.17	−1.55	
3a	+1.27	+0.98	+0.62	+0.26	−1.15	−1.65	
3b	+1.17	+0.93	+0.46	+0.27	−1.12	−1.44	−1.81
3c		+1.01	+0.56	+0.13	−1.03	−1.51	
4a	+1.20	+0.93	+0.62	+0.22	−1.21		
4b	+1.29	+0.94	+0.47	+0.25	−1.14		
4c	+1.27	+0.95	+0.58	+0.13	−1.02		
5a	+1.25	+0.85	+0.44	+0.02	-1.26		
5c	+1.31	+0.92	+0.45	+0.05	−1.02		
6a	+1.21	+0.85	+0.44	+0.03	−1.29	−1.77	
6c	+1.26	+0.89	+0.45	+0.09	−1.09	−1.51	
6d		+0.96	+0.43	+0.14	−0.94	−1.41	−1.82
7a	+1.16	+0.80	+0.40	−0.03			
7c	+1.14	+0.79	+0.33	−0.02			
8a	+1.20	+0.97	+0.61	+0.15			
8c	+1.17	+0.89	+0.43	−0.01			
9a	+1.12	+0.84	+0.24	−0.19			
10b	+1.15	+0.89	+0.31	+0.06			
11a	+1.07	+0.78	+0.35	−0.12			

[a]Obtained in BuCN (**1c**, **2**, **3**, **6**, **7**) or CH₂Cl₂ (**1a**, **4**, **5**, **8–11**) containing 0.1 M Bu₄NPF₆. *E*-values *vs.* FeCp₂/FeCp₂⁺ = 0.19 V; scan rate = 0.1 V s⁻¹. Values are ±0.03 V. [b]For complexes **1a**, and **7–11**, the reduction potentials were not measured.
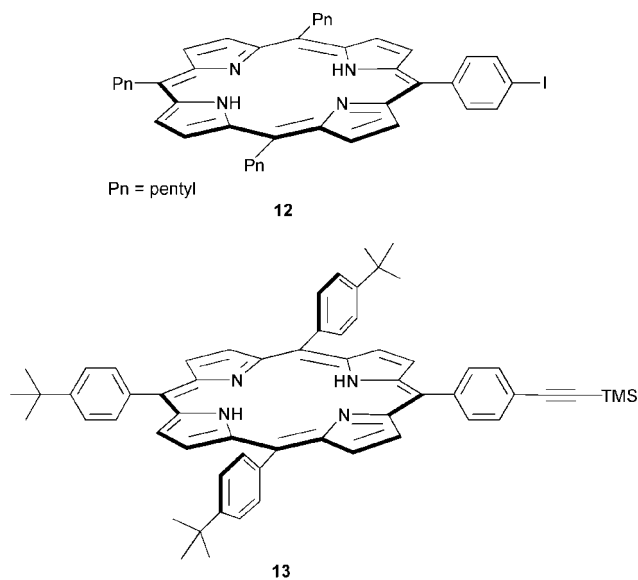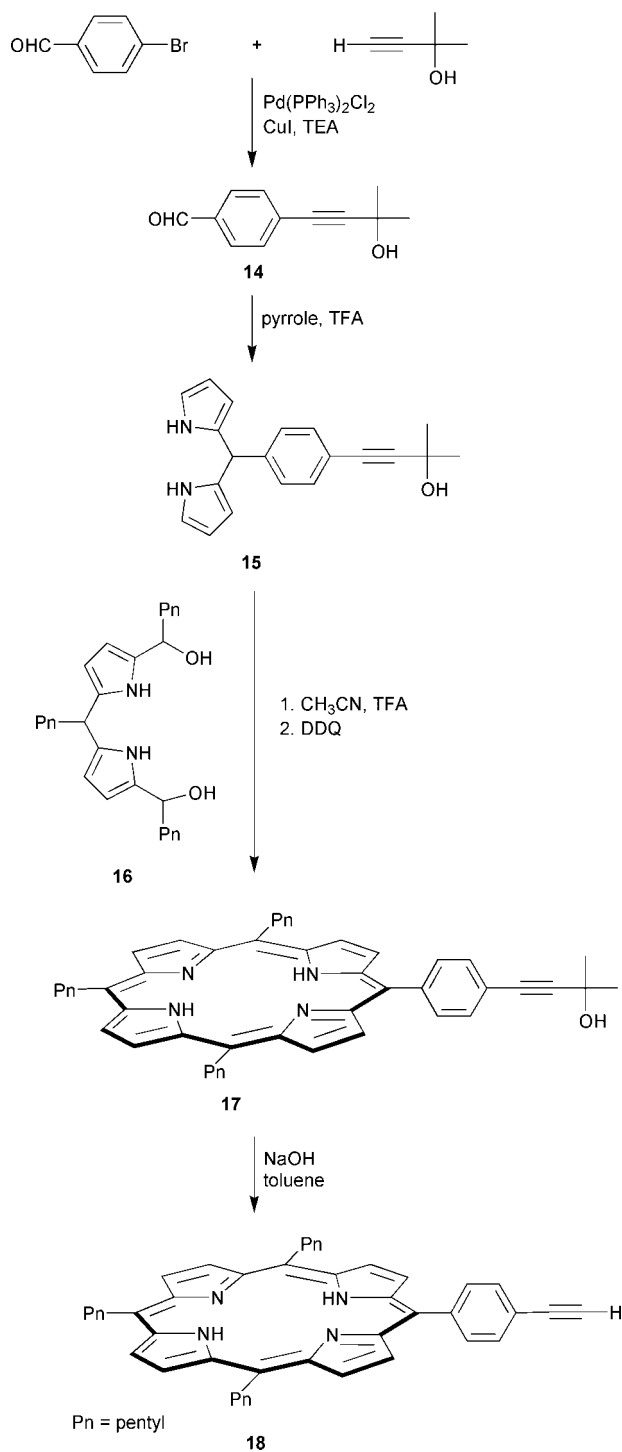
Chart 3

Porphyrin building blocks. The target porphyrins bear one synthetic handle and three non-linking substituents. Such A_3B-porphyrins are readily prepared *via* a new rational synthetic route.[17] A tripentyl mono-iodophenyl porphyrin[6] (**12**) and a tris(4-*tert*-butylphenyl) mono-ethynylphenyl porphyrin[17] (**13**), shown in Chart 3, were prepared *via* this new route. To achieve access to more diverse linkers and substituents as required to prepare suitable combinations of triple deckers, several additional porphyrin building blocks were prepared. The rational synthesis of A_3B-porphyrins requires access to appropriate aldehydes and dipyrromethanes.

The synthesis of a tripentyl mono-ethynylphenyl porphyrin is shown in Scheme 2. The reaction of 4-bromobenzaldehyde and 2-methylbut-3-yn-2-ol under Pd-coupling conditions[21] afforded aldehyde **14**. This rather polar ethyne protecting group was selected in order to facilitate separation of the desired A_3B-porphyrin in the final step of the synthesis. Condensation of **14** with excess pyrrole in the presence of TFA[22] gave dipyrromethane **15** in 56% yield after chromatography followed by recrystallization. The desired dipyrromethane-dicarbinol **16**[17]‡ was prepared in a two-step process and used without further purification. The condensation of dipyrromethane **15** and dipyrromethane-dicarbinol **16** was performed in the presence of TFA in acetonitrile at room temperature followed by oxidation with DDQ.[17] Although this route usually provides a single porphyrin product, dipyrromethane-dicarbinols with aliphatic substituents are known to condense with modest scrambling.[17] In addition to the desired **17**, the major other porphyrin species identified was *meso*-tetrapentylporphyrin. The polarity imparted by the 2-hydroxyisopropyl protecting group enabled facile separation of the mixture, and porphyrin **17** was obtained in 28% yield. Reaction of porphyrin **17** with sodium hydroxide in refluxing toluene[21] proceeded smoothly to give porphyrin **18** in 90% yield.

The synthesis of a thiocyanate-derivatized porphyrin is shown in Scheme 3. Condensation of 7-bromoheptan-1-al[23] with excess pyrrole in the presence of TFA[22] afforded dipyrromethane **19** in 41% yield after chromatography. The condensation of **19** with dipyrromethane-dicarbinol **16** was performed in acetonitrile containing TFA followed by oxidation with DDQ.[17] The desired 6-bromohexylporphyrin **20** was obtained in 34% yield. Treatment of **20** with KSCN furnished
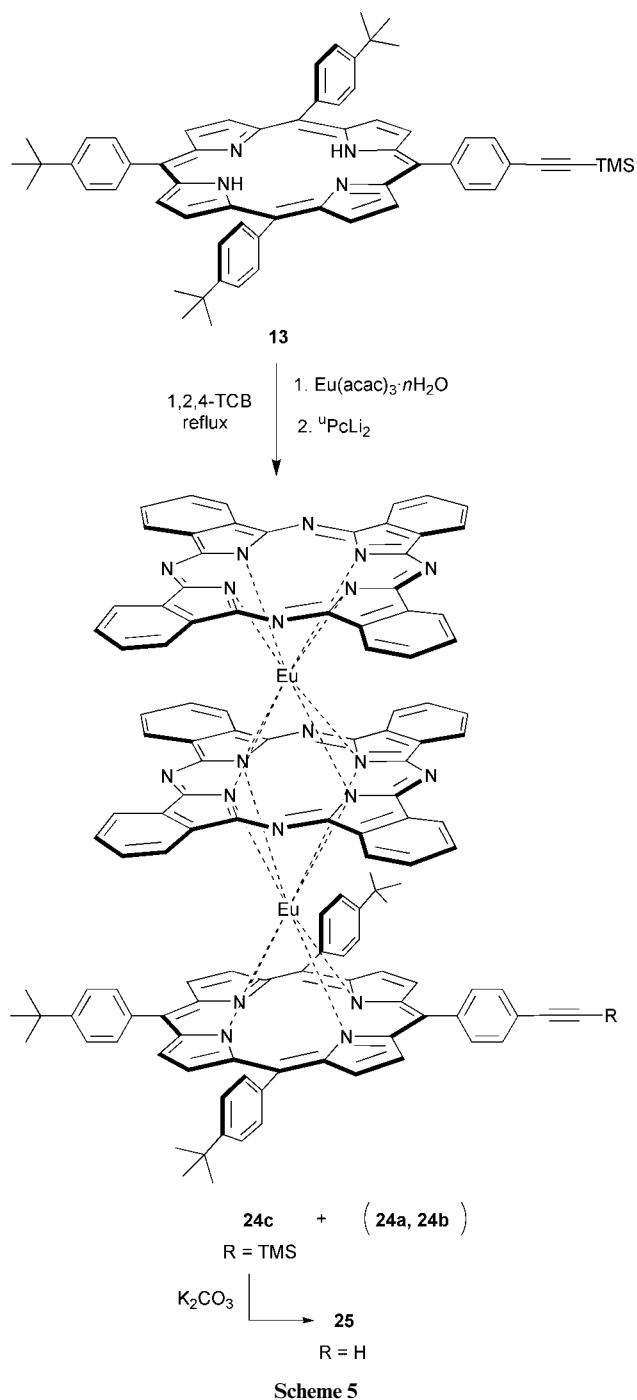
porphyrin **21** bearing a thiocyanate-derivatized linker for attachment to a metal surface.

Triple-decker building blocks. The triple-decker building blocks are exclusively of the c type. Although this triple decker has composition (Pc)Eu(Pc)Eu(Por), we generally aimed to maintain the same ratios of reactants as employed in preparing the library of triple deckers for solution electrochemical studies. This molar ratio of porphyrin : Eu-(acac)$_3 \cdot n$H$_2$O : dilithium phthalocyanine was 1 : 3 : 1.5.[7] The stoichiometric ratio for preparing type-c (or type-b) triple deckers would of course be 1 : 2 : 2; however, the same factors that led to variations in ratios of reactants in preparing the library of triple deckers also led to use of non-stoichiometric ratios in these reactions (see Experimental section).
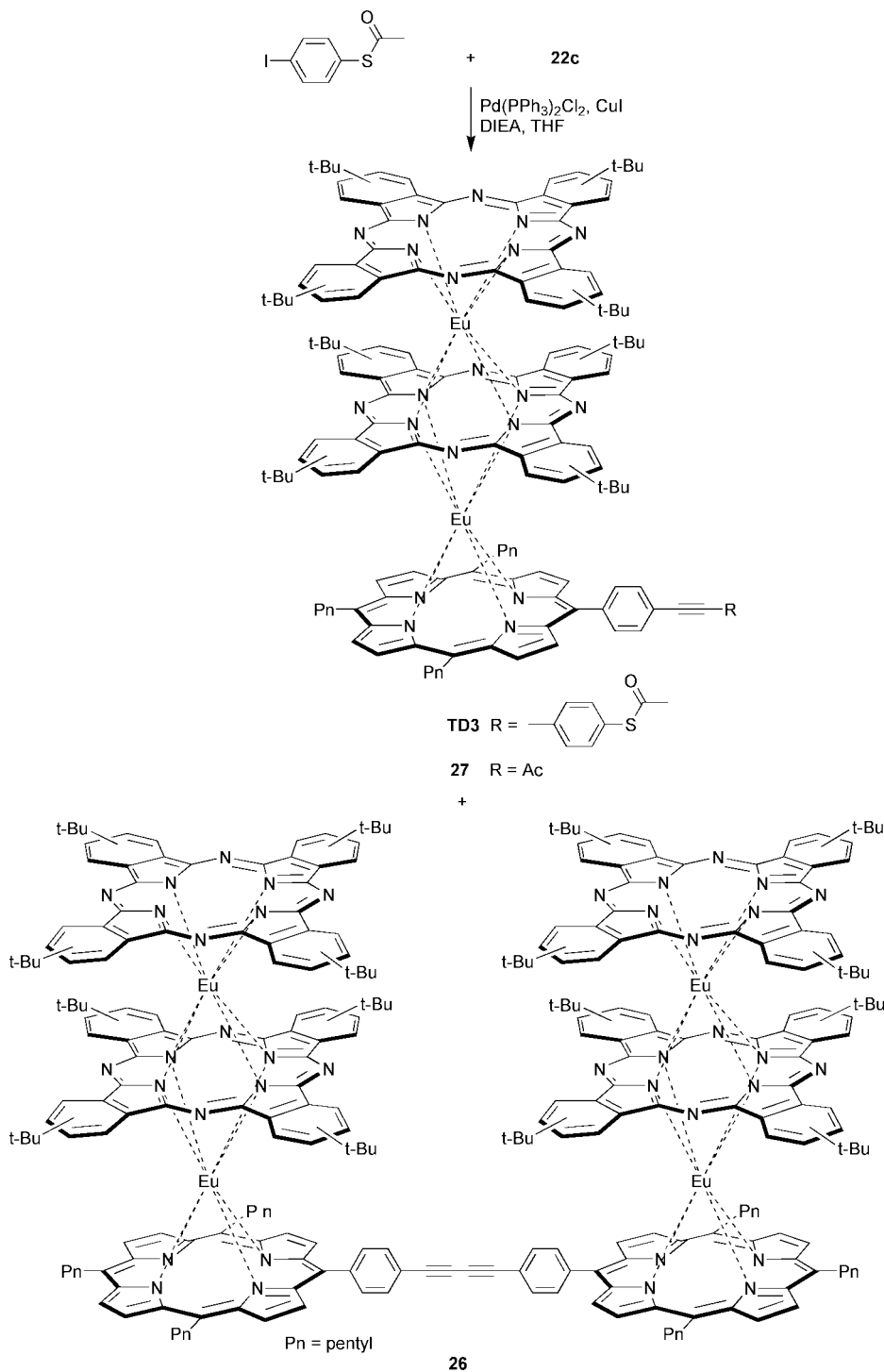
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‡The term carbinol has been abandoned by IUPAC; the IUPAC term for a carbinol is a substituted methanol.

Scheme 2

Scheme 3

18 R = ———≡—H
12 R = I

Pn = pentyl

19

16

20

21

Pn = pentyl

Scheme 3

Pn = pentyl

R = ———≡—H   22c + (22a, 22b)
R = I   23c + (23a, 23b)

Scheme 4

The reaction of Eu(acac)$_3$·nH$_2$O and free base porphyrin **17** afforded the corresponding (Por)Eu(acac) complex. Treatment of the latter with (t-Bu)$_4$PcLi$_2$ in refluxing 1,2,4-trichlorobenzene gave a mixture of six triple deckers (with protected or deprotected ethyne moieties) together with residual starting materials. Because the (2-hydroxyisopropyl)ethyne unit is unstable under the reaction conditions forming the triple decker, we decided to deprotect the ethyne at the porphyrin stage. This approach has the advantage of minimizing synthetic manipulation of the triple deckers.

Thus, free base porphyrin **18** was treated with Eu-(acac)$_3$·nH$_2$O followed by (t-Bu)$_4$PcLi$_2$ in 1,2,4-trichlorobenzene as described above (Scheme 4). Column chromatography of the reaction products on silica with chloroform gave four bands. Further purification of the first band by SEC afforded triple-decker complex **22a** (22%) and unreacted porphyrin **18** (38%). The second band contained free base tetra-*tert*-butylphthalocyanine (5%). The third and fourth bands gave compounds that had identical masses but different absorption spectra. These complexes were assigned as **22b** (1.3%) and **22c** (12%) in order of elution from the adsorption column. A

similar reaction was performed using porphyrin **12** and (t-Bu)$_4$PcLi$_2$. The mono-iodophenyl triple-decker complex **23c** (Scheme 4) was isolated in 12% yield after two column chromatography procedures.

The reaction of free base porphyrin **13** with Eu(acac)$_3$·nH$_2$O followed by ^{u}PcLi$_2$ in refluxing 1,2,4-trichlorobenzene gave a mixture of products together with residual starting materials (Scheme 5). Column chromatography on silica with chloroform gave four bands. Further purification of the first band by SEC afforded triple-decker complex **24a** in 26% yield. The structure was confirmed as the type-a complex by UV-Vis spectroscopy and LD-MS analysis. The third and the fourth bands gave compounds that had identical masses but different absorption spectra. These complexes could be assigned as type-b and type-c complexes [**24b** (1.6%), **24c** (9.1%), respectively] in order of elution from the adsorption column. Treatment of **24c** with K$_2$CO$_3$[24] afforded the deprotected triple decker **25** in 94% yield.

Thiol-derivatized triple-decker complexes. We have investigated several approaches for attaching a thiol handle to triple-decker building blocks *via* a Sonogashira reaction. Our studies have revealed the advantages of certain approaches and conditions for avoiding critical side reactions. These findings have emerged from the following three experiments.

(1) In order to attach a protected thiol unit to the triple decker, ethynyl triple decker **22c** and 1-(S-acetylthio)-4-iodobenzene[2] were reacted under Pd-coupling conditions in

Scheme 5 (left column)

13

1,2,4-TCB reflux

1. Eu(acac)$_3$·nH$_2$O
2. ^{u}PcLi$_2$

24c + (**24a, 24b**)

R = TMS

K$_2$CO$_3$

25

R = H

Scheme 5

Right column

ethynyl triple-decker starting material. We attribute the formation of the acetylated by-product to acetyl transfer from 1-(S-acetylthio)-4-iodobenzene, giving **27**. Related acetyl-transfer reactions have been described recently with S-(acetylthio)-derivatized substituents in the Suzuki reaction.[27]

(2) The difficulties encountered in isolating the desired compound **TD3** prompted the investigation of a complementary route and modified reaction conditions. Formation of the acetylated derivative of the ethynyl triple decker is readily avoided by use of an iodophenyl-substituted triple-decker complex as the starting material. In this case, any acetylation of the ethyne due to side reactions from the S-(acetylthio)benzene starting material would not affect the integrity of the triple-decker product. Furthermore, the omission of copper greatly suppresses homo-coupling. Thus, iodo-substituted triple decker **23c** was reacted with 1-(S-acetylthio)-4-ethynylbenzene[2,28] under the mild copper-free Pd-coupling conditions[29] used for joining porphyrin building blocks [3 mM reactants with P(o-tol)$_3$ and Pd$_2$(dba)$_3$ in toluene–DIEA[26] (5:1) at 35 °C]. After purification, the desired triple decker **TD3** was obtained in 14% yield (Scheme 7), and the unreacted starting material **23c** was recovered in 40% yield. Although the reaction in the absence of copper is slower, the reaction is cleaner facilitating isolation of **TD3**.

(3) The successful reaction in the absence of copper prompted us to reexamine the coupling of an ethynylphenyl triple decker and 1-(S-acetylthio)-4-iodobenzene under these conditions. The ethynylphenyl-substituted triple decker **25** and 1-(S-acetylthio)-4-iodobenzene were coupled under the copper-free Pd-coupling conditions (Scheme 8). LD-MS analysis of the crude reaction mixture revealed two dominant peaks (m/z 2179, 2287) corresponding to the acetylated product and the desired product, respectively. Column chromatography afforded the two separate triple deckers. ^{1}H NMR analysis of the former species revealed a sharp singlet (2.86 ppm, 3H) consistent with an acetyl moiety (**28**). The desired S-(acetylthio)-derivatized triple decker **TD4** was obtained in 19% yield, which is quite low compared with the typical yield ($\sim$50–60%) in the Pd-coupling reaction of two porphyrin monomers, for which these conditions were developed. Thus, excluding copper from the coupling reaction avoids homo-coupling but does not suppress the acetyl-transfer reaction.

Triple-decker complexes bearing thiol-derivatized aliphatic linkers were also prepared to investigate the effect of different linkers on the information storage properties of the electro-active molecules. This approach has the added feature that Pd-coupling reactions are not required to introduce the thiol unit. Thus, the reaction of 6-bromohexylporphyrin **20** with Eu-(acac)$_3$·nH$_2$O followed by ^{u}PcLi$_2$ in 1,2,4-trichlorobenzene gave **29c** in 11% yield (Scheme 9). Treatment of **29c** with KSAc in DMF[30] only led to the recovery of the starting material. The reaction of **29c** with thioacetate was performed in the presence of 18-crown-6[31] in THF for 5 h, affording a triple-decker product in 50% yield. The triple-decker product exhibited the characteristic features expected for **TD5** upon analysis by preparative SEC, TLC, absorption spectroscopy, and ^{1}H NMR spectroscopy. However, LD-MS analysis revealed the expected peak at m/z 2008.4 and an additional peak at m/z 2040.6. The peak ratio was $\sim$4.4:1. A second synthesis performed at slightly larger scale afforded the same two peaks with ratio $\sim$2.4:1. We attribute these two peaks [M$^+$, (M+32)$^+$] to the expected S-(acetylthio)-derivatized triple decker **TD5** and a byproduct containing one additional sulfur atom. The molecular structure of the component giving rise to the (M+32)$^+$ peak is not known, though the following observations are relevant. (1) The reaction of 1.2 equiv. of KSAc with 7-bromoheptanal at high concentration (0.34 M) did not give the corresponding byproduct.[2] (2) A related reaction of 5 equiv. of KSAc with *meso*-tetrakis(3-bromomethylphenyl)-porphyrin at a concentration typical of porphyrin reactions


Lower left column

the presence of copper(I) iodide (Scheme 6).[25] Because the S-acetylthio group can undergo cleavage in the presence of many of the commonly used bases in Pd-coupling reactions, N,N-diisopropylethylamine (DIEA) was used instead of the more typical TEA.[26] No cleavage product was found in the reaction mixture. However, three major components were detected by TLC. The mixture was separated into two fractions by silica column chromatography followed by SEC. The first fraction (less polar) contained one component. Based on molecule ion peak assignments (LD-MS), the structure of this less polar compound was assigned to a butadiyne-linked dyad of triple deckers (**26**). Homo-coupling of ethynes yielding the butadiyne species is a well-known side reaction in Sonogashira reactions in the presence of copper. The second fraction contained two inseparable compounds. The LD-MS spectrum showed two major peaks at m/z 2439 and 2548. The latter corresponds to the desired S-(acetylthio)-derivatized triple decker (**TD3**), while the former is consistent with an acetylated derivative of the

Scheme 6

(5 mM) afforded the corresponding *S*-(acetylthio)-derivatized porphyrin with no $(M+32)^+$ peak observed in the LD-MS spectrum.[19] While this latter reaction employs a benzylic bromide, which is expected to be much more reactive than an alkyl bromide, the absence of the $(M+32)^+$ peak in the LD-MS spectrum suggests the observed peak in the spectrum of the triple-decker product is not a mass spectral artifact. We tentatively assign the $(M+32)^+$ peak to a product with an –S–SAc unit attached to the terminus of the alkyl chain instead of the expected –SAc unit. The origin of this byproduct may stem from the low concentration of the triple decker **29c** (2.5 mM) and the large excess of KSAc (18 equiv.) employed to achieve reaction with the unreactive alkyl bromide. Thus, the triple-decker product **TD5** is not pure and contains a 20–30% impurity of very similar structure to that of **TD5**.

The reaction of the thiocyanate-derivatized porphyrin **21** with Eu(acac)$_3$·nH$_2$O and ^{u}PcLi$_2$ gave the triple decker **TDSCN** in 6% yield. Though the yield is low, this approach introduces the thiol moiety prior to triple-decker formation and thereby avoids synthetic manipulation of the triple decker.

3. Redox properties and charge-retention characteristics of the triple-decker SAMs

Electrochemical properties of the thiol-derivatized triple deckers. The solution electrochemical properties of triple deckers **TD1–5** and **TDSCN** were examined and compared with those of the most structurally similar non-thiol-derivatized complexes. Representative square-wave voltammograms of **TD1** and **TD2** in solution are shown in Fig. 1. The half-wave

Pn = pentyl

TD3
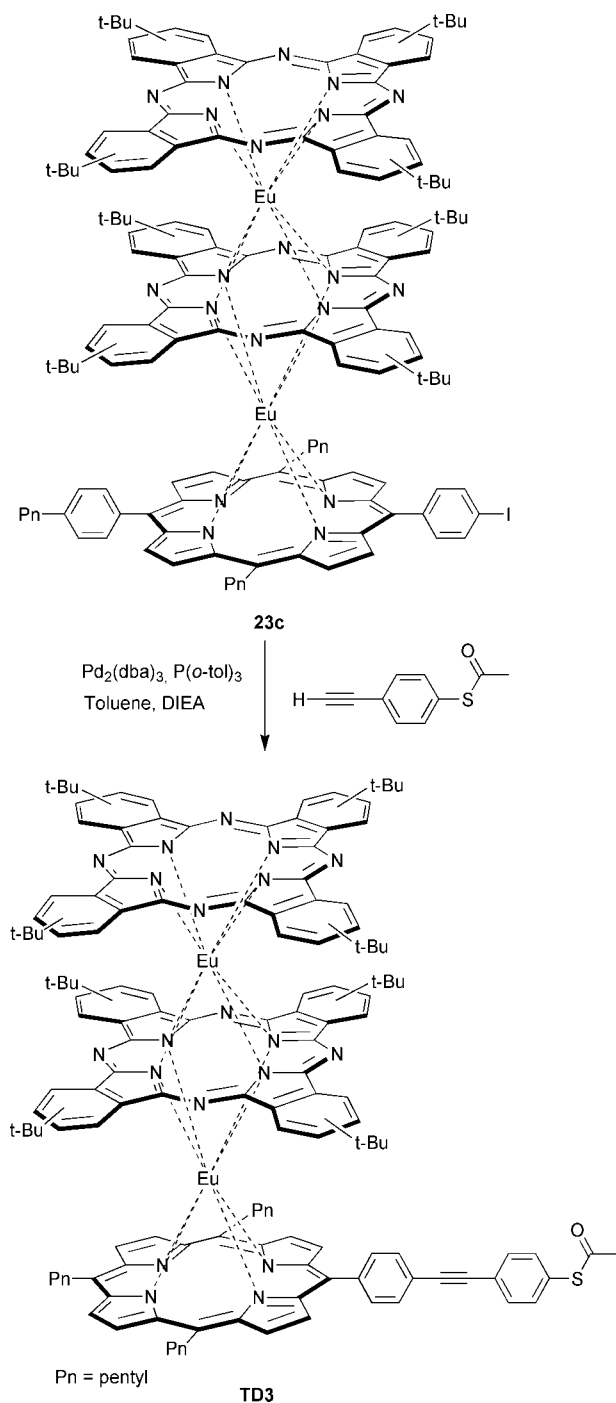
Scheme 7

potentials for all five thiol-derivatized triple deckers are summarized in Table 3. Inspection of the data in Tables 2 and 3 shows that the solution redox potentials of **TD1**, **TD2**, **TD3**, **TD4** and **TD5** are quite similar to those of the triple deckers **1c**, **7c**, **6c**, **4c**, and **5c**, respectively. The electrochemical properties of **TDSCN** are similar to those of **TD5** (not shown). In all cases, the potentials for the analogous states of the thiol-derivatized *versus* (most structurally similar) non-derivatized triple deckers differ by 0.1 V or less. The largest differences in potential (albeit small) occur for **TD3** and **TD2** where one of the *meso*-pentyl substituents of the parent non-derivatized porphyrin is replaced by the *S*-(acetylthio)diarylethyne linker. The potential differences are negligible for the other three thiol-derivatized *versus* non-derivatized triple deckers because the *S*-(acetylthio)diarylethyne [or *S*-(acetylthio)hexyl] linker has very similar electron-donating properties to the aryl (or pentyl) group of the parent triple decker.

Each thiol-derivatized triple decker was examined for formation of a SAM on a Au microelectrode. The *S*-acetylthio group is known to undergo cleavage *in situ* on Au.[19,20] The electrochemical behavior of the thiol-derivatized triple-decker SAMs was investigated. In the case of **TD1–5** (*S*-acetyl protecting group), high quality voltammograms were obtained for the SAMs. On the other hand, **TDSCN** did not appear to form a SAM, as evidenced by the absence of any discernible redox behavior on the Au microelectrode. No further attempts were made to elicit SAM formation for **TDSCN**.

Representative fast-scan (100 V s^{-1}) voltammograms of the SAMs prepared from **TD1** and **TD2** are shown in Fig. 2. The voltammograms for the SAMs derived from **TD3**, **TD4**, and **TD5** are similar (not shown). The SAMs of the various complexes do not exhibit any appreciable change in redox characteristics after a large number (thousands) of oxidation/reduction cycles. The electrochemical robustness of the triple-decker SAMs is similar to that previously observed for SAMs of monomeric porphyrins, multiporphyrin arrays, and other triple deckers.[1–6] We note that despite the presence of an impurity in **TD5**, this triple decker formed a SAM that exhibits a single set of oxidation waves. This behavior is consistent with the impurity being either (1) a complex that cannot bind to Au, or (2) a complex wherein the triple decker and protecting group are joined *via* an S–S bond (*vide supra*). Disulfide linkages are known to undergo facile cleavage upon exposure to Au.[32]

The half-wave potentials for the triple-decker SAMs are compared in Table 3 with those observed in solution. Inspection of the data shown in Fig. 2 and Table 3 reveals that each of the triple-decker SAMs exhibits four reversible oxidation waves. Each of the potentials for all of the triple-decker SAMs is shifted more positive than the analogous potential for a given complex in solution. This behavior is consistent with that previously observed for SAMs of various porphyrins.[1–6] Positive shifts in redox potential have also been observed upon SAM formation of other electroactive species (*e.g.*, thiol-derivatized ferrocenes) on Au.[33] For the triple deckers, the magnitude of the potential shift in the SAMs *versus* solution ranges from ∼0.05 to ∼0.35 V. There are no clear trends in the potential shifts except that the shifts for the higher oxidation states are generally larger than those for the lower oxidation states (see Table 3). This behavior is qualitatively consistent with the proposed mechanism of SAM-induced potential shifts. In particular, the positive shifts have been attributed to the fact that in a well-packed monolayer, counter ions cannot as effectively access the redox center and screen charge.[33] Thus, highly oxidized species would be expected to be more destabilized in the SAM than species carrying lower charge.

Finally, we note that in our previous study of the electrochemical behavior of triple-decker SAMs, only three of the four oxidation waves could be observed.[6] The fourth wave was not visible because the electrochemical window terminated at ∼1.3 V. In our current studies, the fourth wave is clearly visible because the electrochemical window has been extended to ∼1.6 V. We attribute the extension of the electrochemical window to a much more rigorous exclusion of water from solvents, electrolyte, and the Au surface prior to SAM formation. Regardless, the ability to observe the fourth oxidation state in the triple-decker SAM is important for maximizing the amount of information that can be stored in a multibit element.

Charge-retention characteristics of the triple-decker SAMs. The ability to retain charge in the absence of applied potential is a key property of any molecular-based information storage system. A long charge-retention time simultaneously increases the time between refresh cycles (thereby enabling a memory element to be accessed for a larger fraction of time) and also reduces total power consumption of the system. In this
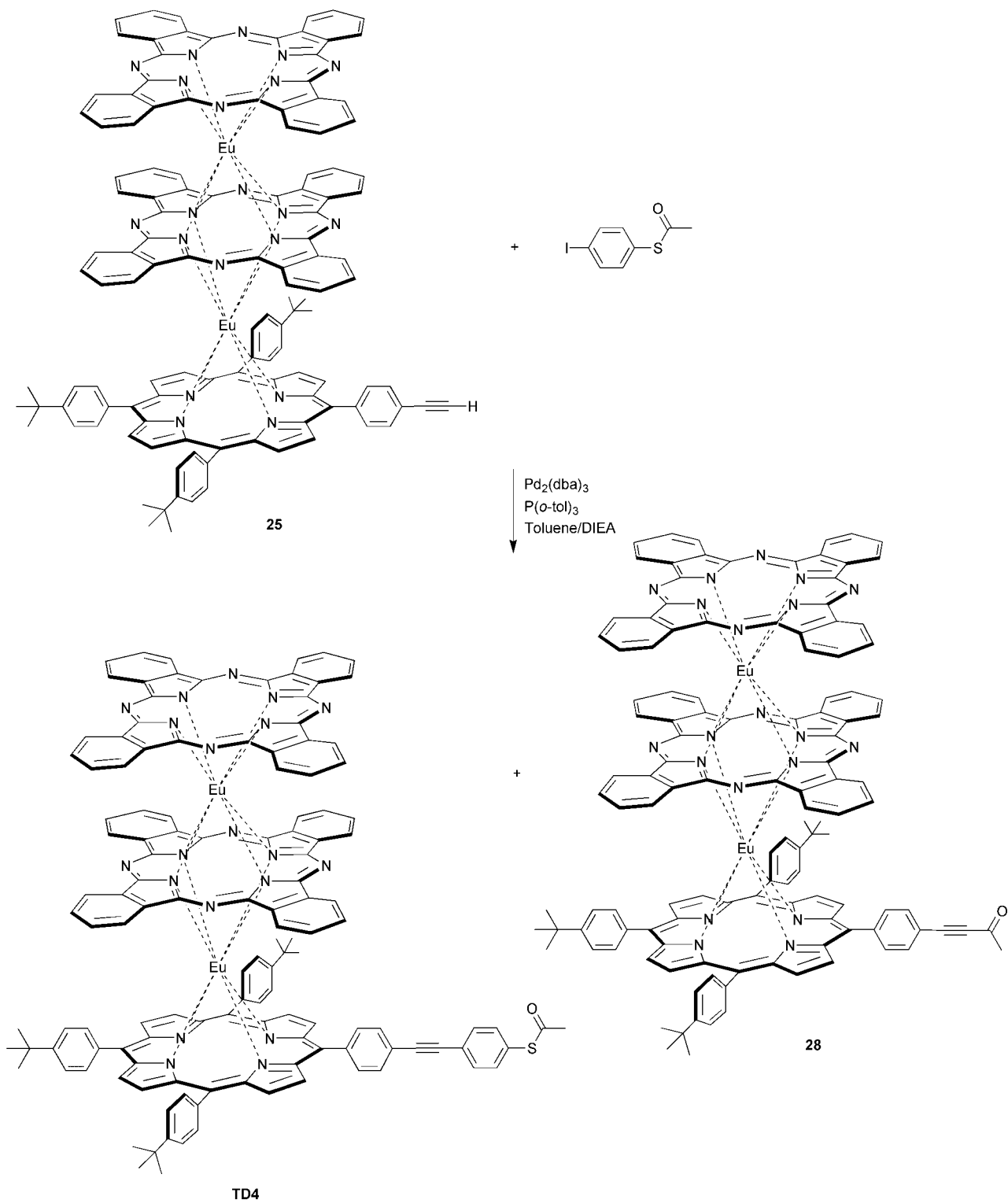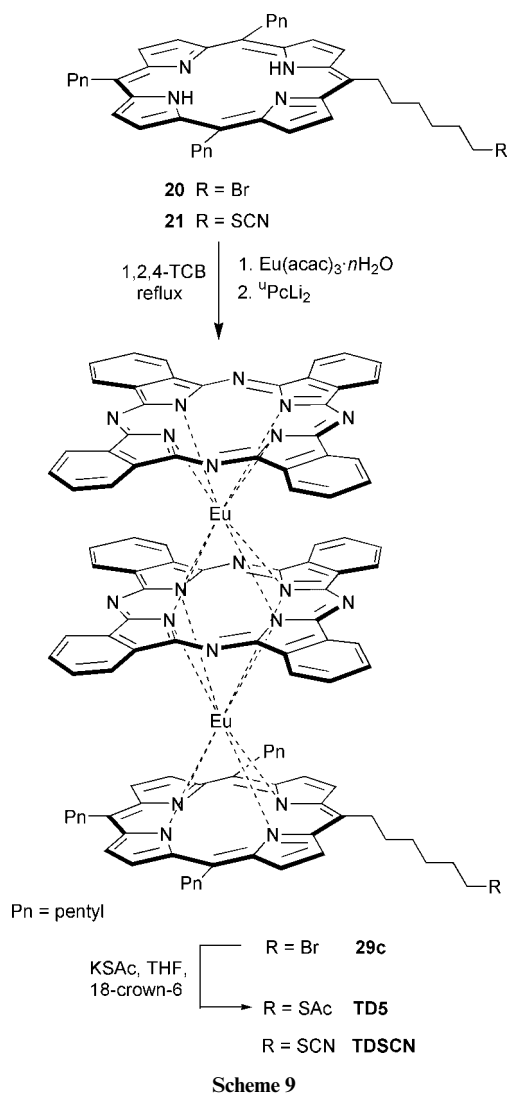
Scheme 8

regard, we have previously shown that SAMs of monomeric porphyrins retain charge for up to hundreds of seconds after disconnection from the source of applied potential.[1] This time is several orders of magnitude longer than a semiconductor-based dynamic random access memory (DRAM) element. Accordingly, we sought to investigate the charge-retention characteristics of the various redox states of the triple-decker SAMs.

The charge-retention characteristics of the five different triple-decker SAMs were measured using the same procedures we have previously employed for SAMs of monomeric porphyrins (see Experimental section).[1,34] These methods

determine the amount of charge retained in the oxidized SAM at a series of times after disconnection from the source of applied potential. Representative data sets are shown for the SAM of **TD1** in Figs. 3 and 4. Fig. 3 displays the reductive current measured at times of 10 s (top trace), 60 s (middle trace), and 100 s (bottom trace) following reconnection of the system (wherein the molecules in the SAM that have remained oxidized are reduced). The four panels in Fig. 3 display the current transients observed for each of the four oxidation states of the triple decker (State 1, $E_1 \rightarrow E_0$; State 2, $E_2 \rightarrow E_0$; State 3, $E_3 \rightarrow E_0$; State 4, $E_4 \rightarrow E_0$). Fig. 4 displays the total charge retained in the SAM at a disconnect time of 60 s. These curves

20 R = Br
21 R = SCN

1,2,4-TCB
reflux

1. Eu(acac)₃·nH₂O
2. ᵘPcLi₂

Pn = pentyl

KSAc, THF,
18-crown-6

R = Br   **29c**
R = SAc   **TD5**
R = SCN   **TDSCN**

Scheme 9

are obtained by integrating the data shown in the middle traces in each panel of Fig. 3. The data obtained for the other four triple-decker SAMs (not shown) are similar to those shown for **TD1**.

For all five triple-decker SAMs, the decay of the charge (*i.e.*, integrated current) as a function of disconnect time fits a first-order rate law with high fidelity ($r^2 \sim 0.98$) for each of the four oxidation states. First-order kinetic behavior is not necessarily expected for charge decay from the higher oxidation states, but is similar to that previously observed for charge decay from the second oxidation state of SAMs of monomeric porphyrins.[1,34] In principle, a sequential depletion of charge (*i.e.*, $E_n \rightarrow E_{n-1} \ldots \rightarrow E_0$) should result in multi-exponential decay. However, the charge decay from the higher oxidation state of the porphyrin SAMs (both triple deckers and monomers) exhibits pseudo first-order kinetics. We are currently in the process of analyzing this behavior in more detail. Regardless, the observation of pseudo first-order kinetic behavior permits the determination of a half-life ($t_{\frac{1}{2}}$) for charge retention. The $t_{\frac{1}{2}}$ values are particularly convenient parameters for characterizing the charge-retention characteristics of the SAMs.

The $t_{\frac{1}{2}}$ values for the five triple deckers are listed in Table 4. The charge at time = 0 s (extrapolated from the fit of the decay curves), corresponding to the total charge that can be placed on the molecules in the SAM, is also listed in the table. These values are listed as charge densities (σ_0) in order to permit comparison of measurements made with different electrodes (which have somewhat different areas). Inspection of the data shown in Table 4 reveals the following:
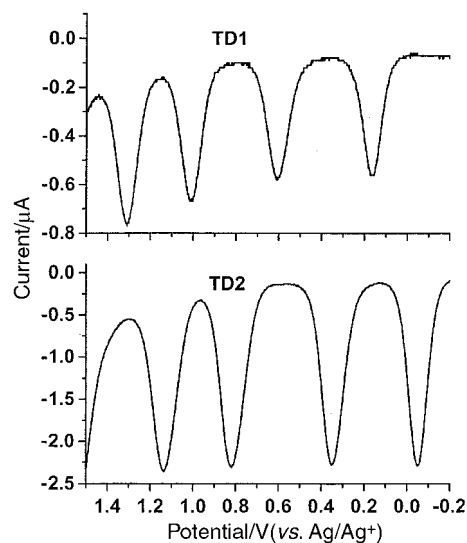
(1) Each of the four oxidation states of all five triple deckers retains charge for times of tens of seconds or more. The exact $t_{\frac{1}{2}}$ value for a given oxidation state varies depending on the triple decker. Regardless, in all cases, the $t_{\frac{1}{2}}$ value for the lowest oxidation state is the shortest, while that for the highest oxidation state is the longest. In addition, the $t_{\frac{1}{2}}$ value monotonically increases as the oxidation state increases. This behavior is similar to that previously observed for the first and second oxidation states of monomeric porphyrin SAMs.[34]

(2) The σ_0 values vary considerably among the different triple deckers. However, in all cases the amount of stored charge monotonically increases as the oxidation state increases. Ideally, the σ_0 value would increase linearly as a function of the oxidation state. Such behavior is qualitatively observed for the SAM of **TD1**, but not for the other complexes. Regardless, the observation that the amount of stored charge in the triple-decker SAMs systematically increases as a function of oxidation state is consistent with the behavior we have previously observed for monomeric porphyrin SAMs.[34]

(3) The $t_{\frac{1}{2}}$ and σ_0 values for the SAM of **TD5** (hexyl linker) are in the same general range as those for the SAMs of **TD1–4** (diarylethyne linker). The observation that the charge retention and storage characteristics of triple deckers containing these two types of linkers are similar is qualitatively consistent with the behavior exhibited by monomeric porphyrins containing these same linkers.[35] However, the $t_{\frac{1}{2}}$ values for the triple deckers are in general shorter than those of the SAMs of monomeric porphyrins. For example, the $t_{\frac{1}{2}}$ value for the first oxidation state of each triple decker is in the range of 10–20 s (Table 4), whereas the $t_{\frac{1}{2}}$ value for the first oxidation state of a monomeric porphyrin containing a *meso*-diarylethyne linker or *meso*-hexyl linker is 51 or 41 s, respectively.[35] A different choice of linker could potentially increase the $t_{\frac{1}{2}}$ values for the triple deckers. In this regard, our previous studies of porphyrin monomers bearing diverse linkers reveal that the charge-retention times can be altered by at least 10-fold by structural modification of the linker. Similar studies concerning the effects of linker length and composition on charge-retention times of triple deckers will be the subject of future investigations.

(4) Examination of the structures of the constituent porphyrins and phthalocyanines in the triple-decker complexes reveals no obvious relationship between the $t_{\frac{1}{2}}$ and/or σ_0 values and the structure of the building blocks. For example, **TD1** (unsubstituted phthalocyanines and a porphyrin with one phenyl and two *p*-tolyl groups as non-linking substituents) has relatively low σ_0 values compared with **TD4** (unsubstituted

Table 3 Half-wave potentials for thiol-derivatized triple-decker complexes in solution *vs.* SAMs[a]

| Triple decker | Half-wave potential | | | | | | | |
| | $E_{0/+1}$ | | $E_{+1/+2}$ | | $E_{+2/+3}$ | | $E_{+3/+4}$ | |
	Soln	SAM	Soln	SAM	Soln	SAM	Soln	SAM
TD1	0.16	0.34	0.61	0.76	1.01	1.15	1.31	1.44
TD2	−0.05	0.12	0.35	0.52	0.82	0.99	1.13	1.34
TD3	0.04	0.11	0.47	0.52	0.94	1.03	1.28	1.43
TD4	0.16	0.42	0.59	0.85	0.97	1.25	1.29	1.58
TD5	0.09	0.40	0.46	0.74	0.93	1.16	1.32	1.57

[a]Obtained in CH_2Cl_2 containing 0.1 M Bu_4NPF_6. *E*-values *vs.* $FeCp_2/FeCp_2^+ = 0.19$ V; scan rate $= 0.1$ V s^{-1} (soln); 100 V s^{-1} (SAM). Values are ± 0.03 V.

phthalocyanines and a porphyrin with three *p-tert*-butylphenyl groups) despite the similarities in the substituents. The same is also the case for **TD2** (β-octamethylphthalocyanines and a porphyrin with three *meso*-pentyl groups) compared with **TD3** (β-tetra-*tert*-butylphthalocyanines and a porphyrin with three

Fig. 2 Fast-scan voltammetry of the SAM of **TD1** and the SAM of **TD2**. The solvent overlayer was CH_2Cl_2 containing 0.1 M Bu_4NPF_6; scan rate 100 V s^{-1}.

Fig. 3 Current-decay transients for the SAM of **TD1**. The three traces shown in each panel are the reductive current measured using the OCPA method (see Experimental section). The traces were obtained 10 s (top trace), 60 s (middle trace), and 100 s (bottom trace) after disconnection from the source of applied potential. The four panels depict the charge-decay of the four different oxidized states to the neutral state ($E_n{\rightarrow}E_0$, $n = 1, 2, 3, 4$).

meso-pentyl groups). The appearance of the voltammograms for the various triple deckers does not lend any insight into this issue. For all the triple deckers examined, the voltammograms are equally well resolved and do not provide any evidence that structural inhomogeneities might exist in the monolayer that would yield differential surface coverage and/or charge-storage characteristics. A detailed understanding of these issues will require the screening of a much larger library of SAMs of thiol-derivatized triple deckers.
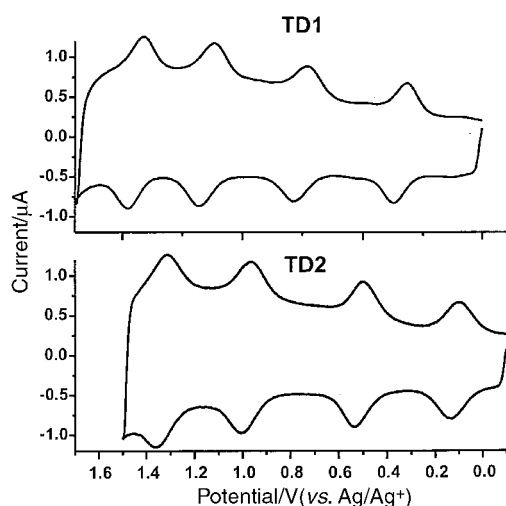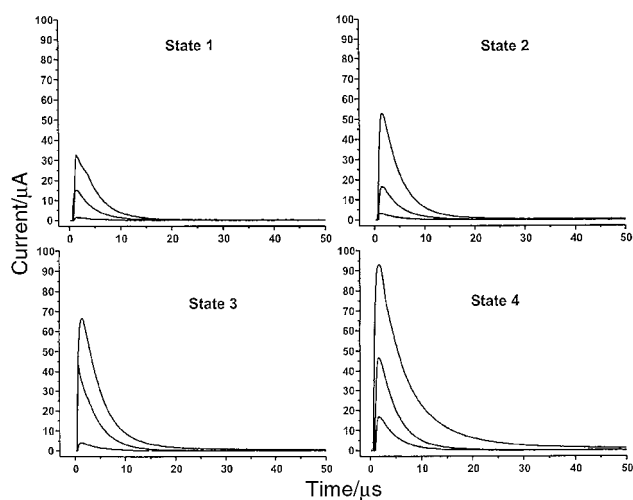
Electrochemical characteristics of mixed monolayers of triple deckers. One of the original goals of our study of triple deckers was to construct a system that would "count to eight." Examination of the half-wave potentials for the SAMs of the five thiol-derivatized triple deckers (Table 3) reveals that mixed SAMs of **TD1** or **TD4** with any of the other three triple deckers should yield a system in which the four oxidation waves of the two components are interleaved. Towards this end, we performed a number of co-deposition experiments with the various triple deckers. The mixed SAM of **TD2** and **TD4** is shown in Fig. 5. In all cases, the molecules appeared to partition approximately equally as evidenced by the relative amplitudes of the oxidation waves in the cyclic voltammograms. Typically, the oxidation waves from all eight states were visible in the mixed SAM. However, the waves were very poorly resolved, more so than would be expected from superimposing the voltammograms of the individual triple-decker SAMs. These observations suggest the mixed SAMs are much more inhomogeneous than are the SAMs of the neat triple deckers. Owing to the poor resolution of the oxidation waves in the mixed SAMs, we could not perform charge-retention measurements that would reliably address a specific oxidation state of the system.
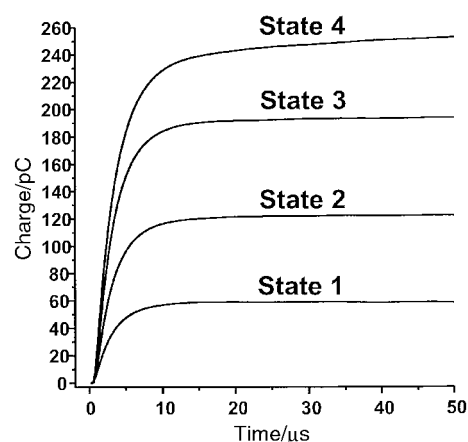

Fig. 4 Integrated current-decay transients for the SAM of **TD1**. The four traces shown are for the 60 s trace shown in Fig. 3.
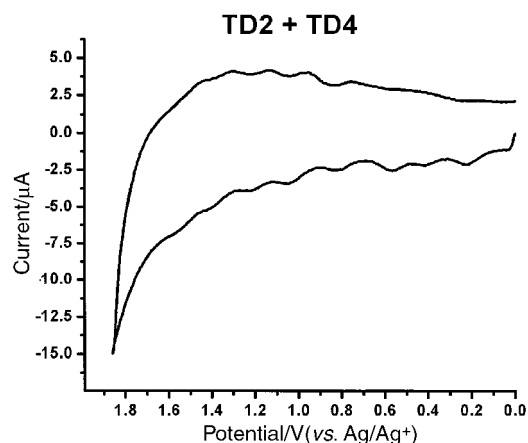
Fig. 5 Fast-scan voltammetry of the mixed SAM of **TD2** and **TD4**. The solvent overlayer was CH_2Cl_2 containing 0.1 M Bu_4NPF_6; scan rate 100 V s^{-1}.

Conclusion

A library of triple-decker complexes comprised of different porphyrins and phthalocyanines bearing various electron-donating substituents has been synthesized. As part of the synthesis effort, a suitable route for attaching a thiol linker to a triple decker complex has been identified that avoids some problematic side reactions. This route employs an iodophenyl- rather than an ethynylphenyl-substituted triple-decker complex. Electrochemical examination of the library of triple deckers has revealed substituents that shift the oxidation states to the low potential regime. In addition, appropriate pairs of these compounds have been identified that may be used in the design of an octal counter. Four new thiol-derivatized triple-decker complexes have been prepared. Each of the *S*-(acetylthio)-derivatized complexes forms a SAM on Au that exhibits robust, reversible electrochemistry. Altogether, five triple deckers (two prepared previously, three prepared herein) have been used to form SAMs. Each of the four accessible oxidation states of the triple-decker SAMs retains charge for tens of seconds or more in the absence of applied potential. Thus, these complexes appear to be excellent candidates for multibit information storage elements. However, mixed SAMs of the triple deckers do not exhibit optimum electrochemical behavior for use as a prototypical octal counter. Accordingly, we are currently in the process of synthesizing covalently linked dyads of triple-decker complexes with the appropriate half-wave potentials to achieve this goal.

Experimental

General

All ^{1}H NMR spectra were collected in $CDCl_3$ (300 MHz) unless noted otherwise. All absorption spectra (HP 8451A, Cary 3) were collected in toluene unless noted otherwise. The triple-decker sandwich complexes were analyzed by laser desorption mass spectrometry (LD-MS; Bruker Proflex II) and high resolution fast atom bombardment mass spectrometer (FAB-MS; JEOL HX 110HF). LD-MS analysis was done without a matrix[12] or with the matrix 1,2-bis(5-phenyloxazol-2-yl)benzene (POPOP). High resolution mass spectrometry was carried out at greater than unit resolution.

Chromatography

Adsorption chromatography was performed using flash silica (Baker, 60–200 mesh). Preparative size exclusion chromatography (SEC) was performed using BioRad Bio-beads SX-1.[29] Analytical SEC was performed with a Hewlett-Packard 1090 HPLC using a 1000 Å column (5 μL, styrene-divinylbenzene copolymer) with THF as eluant (0.8 mL min^{-1}).[29]

Solvents and reagents

Toluene was distilled from CaH_2, THF (Fisher, certified ACS) was distilled from sodium–benzophenone, and triethylamine (Fluka, puriss) was distilled from CaH_2. Pyrrole (Acros) was distilled at atmospheric pressure from CaH_2. All other solvents were used as received. Eu(acac)$_3$·nH$_2$O was obtained from Alfa Aesar. Unless otherwise indicated, all other reagents were obtained from Aldrich Chemical Company, and all solvents were obtained from Fisher Scientific. The phthalocyanines (*t*-Bu)$_4$PcH$_2$ and (octyloxy)$_8$PcH$_2$ were obtained from Aldrich; (heptyl)$_8$PcH$_2$[36] was obtained as a by-product during syntheses of a mono-ethynyl hexaheptylphthalocyanine;[37] (Me)$_8$PcH$_2$ was obtained as described in the literature.[38]

Dilithium phthalocyanines

Dilithium phthalocyanine was obtained from Aldrich (dye content ∼70%). The other dilithium phthalocyanine derivatives were prepared following a standard method: The parent phthalocyanine was treated with excess (∼2-fold) lithium pentoxide in pentanol at 140 °C for a few hours. The reaction was monitored by absorption spectroscopy. Upon completion, the solvent was removed under vacuum. The residue was extracted with dry acetone in a Soxhlet extractor until the extracting solvent was nearly colorless, which typically required about 4 h. The resulting solid was stored under argon. The dilithium phthalocyanines were used without further purification. The number of moles of a PcLi$_2$ compound is taken to be 70% for a given mass of ^{u}PcLi$_2$ and 100% for all other dilithium phthalocyanines (though the purity of the dilithium derivatives of the substituted phthalocyanines was not determined).

General procedure for the preparation of triple deckers

Following a general procedure[9,10] with molar ratios as described,[7] a mixture of the porphyrin (0.060 mmol) and Eu(acac)$_3$·nH$_2$O (0.18 mmol) in 1,2,4-trichlorobenzene (13 mL) was heated to reflux and stirred under argon for 4 h. The resulting cherry-red solution was cooled to room temperature, then the dilithium phthalocyanine (0.090 mmol)

Table 4 Charge densities and charge-retention half-lives for thiol-derivatized triple-decker complexes in SAMs^a

Triple decker	State 1		State 2		State 3		State 4	
	σ_0	$t_{\frac{1}{2}}$	σ_0	$t_{\frac{1}{2}}$	σ_0	$t_{\frac{1}{2}}$	σ_0	$t_{\frac{1}{2}}$
TD1	0.14	21	0.25	32	0.64	89	0.95	130
TD2	0.18	16	0.44	27	0.79	60	1.1	75
TD3	0.80	8.6	1.1	13	1.3	30	1.5	90
TD4	0.88	10	1.3	19	1.9	34	2.9	58
TD5	0.12	27	0.18	37	0.40	80	0.60	91

^{a}Charge density at $t=0$ s (σ_0/μC cm^{-2}) and charge-retention half-life ($t_{\frac{1}{2}}$/s) obtained by fitting the decay in the observed charge *vs.* disconnect time to a first-order rate law.

was added. The mixture was refluxed for an additional 5 h, then the volatile components were removed under vacuum. The residue was dissolved in CHCl₃ and chromatographed (silica, CHCl₃) affording three main bands. The first band (brown) contained predominantly the type-a triple-decker complex (Por)Eu(Pc)Eu(Por) and unreacted porphyrin starting material. The second main band (olive or black) contained the type-b triple-decker complex (Pc)Eu(Por)Eu(Pc) in a very small amount, which often was not isolated or characterized. The third main band (dark green) contained the type-c triple-decker complex (Pc)Eu(Pc)Eu(Por). The first band (brown) from the silica column was redissolved in THF or toluene and purified by SEC, affording (Por)Eu(Pc)Eu(Por) as the first band (greenish-brown). Removal of the solvent afforded a brownish-black solid. The third band (dark green) from the silica column was chromatographed again (silica, toluene), affording (Pc)Eu(Pc)Eu(Por) as a dark greenish-blue band. Removal of the solvent afforded a dark green solid.

Notes concerning the triple-decker forming reaction:

(1) All yield calculations are based on the amount of the starting porphyrin.

(2) For Eu(acac)₃·nH₂O, the value of n was assumed to be 3 for calculating the quantity of material in the reactions.

(3) The factors that led to a particular ratio of reactants include (i) availability and purity of the PcLi₂, and (ii) ease of separation of the desired triple decker. The latter issue is particularly critical for obtaining the type-c triple deckers (e.g., the triple-decker building blocks). As previously discussed,[6] the triple-decker forming reaction affords five main products: two double deckers [(Por)Eu(Pc), (Pc)Eu(Pc)] and the three types of triple deckers. The type-c triple decker and the (Pc)Eu(Pc) elute on adsorption chromatography as the fourth and fifth bands, respectively. A stoichiometric ratio of reactants for preparing the type-c (or b) triple deckers would be anticipated to yield a larger amount of the undesired (Pc)Eu(Pc). The ratio of reactants employed in each case was a compromise among these various factors. For example, the impure dilithium phthalocyanine Me₈PcLi₂ was employed in larger quantity in the syntheses of 7–9. On the other hand, the lack of sufficient quantity of NcLi₂ resulted in use of a limiting amount in the synthesis of 11.

Reaction of H₂TTP and (octyloxy)₈PcLi₂ affording triple deckers 2a and 2c

The reaction of H₂TTP (12 mg, 0.017 mmol), Eu(acac)₃·nH₂O (26 mg, 0.052 mmol) and (octyloxy)₈PcLi₂ (40 mg) in 1,2,4-trichlorobenzene (4 mL) afforded four main bands after column chromatography (silica, CHCl₃). The first band (brownish-red) was further purified by SEC (THF). The first band from the SEC column was further purified by chromatography (silica, hexanes–ethyl acetate from 9:1 to 7:3), affording a brown solid (2a, 12 mg, 42%): ¹H NMR (CDCl₃) δ 1.25 (t, J = 7.2 Hz, 24H), 1.7–2.0 (m, 32H), 2.13 (qnt, J = 7.5 Hz, 16H), 2.37 (qnt, J = 7.2 Hz, 16H), 2.79 (m, 16H), 3.11 (s, 24H), 3.36 (m, 16H), 4.29 (s, 16H), 5.17 (d, J = 6.6 Hz, 8H), 6.0–6.2 (m, 16H), 6.79 (d, J = 6.6 Hz, 8H), 9.1–9.3 (m, 8H), 12.10 (s, 8H), 12.83 (s, 8H); LD-MS obsd 3183.7; FAB-MS obsd 3179.54, calcd exact mass 3179.54 (C₁₉₂H₂₁₆N₁₆O₈Eu₂); λ_abs 374, 419, 496, 611 nm. The fourth band (dark green) was purified twice more by column chromatography [silica, toluene; silica, hexanes to hexanes–THF (4:1)], affording a green solid (2c, 8 mg, ~11%): ¹H NMR (CDCl₃) δ 1.01 (t, J = 6.9 Hz, 24H), 1.15 (t, J = 7.1 Hz, 24H), 1.4–1.6 (m, 32H), 1.6–1.9 (m, 80H), 1.9–2.3 (m, 48H), 2.5–2.8 (m, 32H), 3.09 (s, 12H), 3.31 (br s, 16H), 4.95 (br s, 8H), 5.17 (m, 4H), 5.7–6.1 (m, 12H), 6.43 (m, 8H), 6.70 (d, J = 6.6 Hz, 8H), 9.31 (s, 8H), 13.12 (s, 8H); LD-MS obsd 4047.3; FAB-MS obsd 4048,3, calcd exact mass 4048.4 (C₂₄₀H₃₂₄N₂₀O₁₆Eu₂); λ_abs 373, 423, 540, 631, 737 nm.

Reaction of H₂TTP and (t-Bu)₄PcLi₂ affording triple deckers 3a, 3b, and 3c

The reaction of porphyrin H₂TTP (31 mg, 0.046 mmol), Eu(acac)₃·nH₂O (81 mg, 0.16 mmol) and (t-Bu)₄PcLi₂ (45 mg) in 1,2,4-trichlorobenzene (12 mL) gave four main bands after column chromatography (silica, CHCl₃). The first band (brownish-red) was further purified by SEC (THF). The first band (greenish-brown) from the SEC column was further purified by chromatography (silica, hexanes–ethyl acetate from 9:1 to 7:3) affording a brown solid (3a, 7 mg, ~13%): ¹H NMR (CDCl₃) δ 3.0–3.1 (m, 24H), 3.1–3.3 (m, 36H), 4.07 (d, J = 5.7 Hz, 16H), 4.91 (q, J = 8.1 Hz, 8H), 6.5–6.7 (m, 8H), 9.0–9.1 (m, 8H), 10.7–10.9 (m, 4H), 12.0–12.3 (m, 8H), 12.5–13.0 (m, 8H); LD-MS obsd 2388.0, 1562.7, 1547.2, 823.4; FAB-MS obsd 2378.72, calcd exact mass 2378.83 (C₁₄₄H₁₂₀N₁₆Eu₂); λ_abs 362, 421, 493, 608 nm. The second band was further purified by chromatography (silica, toluene), affording a greenish-black solid. Final purification by SEC (THF) afforded a black solid (3b, 2.9 mg, 2.7%): LD-MS obsd 2453.6; λ_abs 346, 417, 526, 620, 727 nm. The fourth band (greenish-black) was further purified by chromatography (silica, toluene), affording a black solid (3c, 19 mg, 17%): The ¹H NMR spectrum (CDCl₃) was collected but the mixture of regioisomers prevented interpretation. LD-MS obsd 2449.5; FAB-MS obsd 2447.05, calcd exact mass 2446.94 (C₁₄₄H₁₃₂N₂₀Eu₂); λ_abs 346, 417, 526, 620, 727 nm.

Reaction of H₂TBP and ᵘPcLi₂ affording triple deckers 4a, 4b, and 4c

The reaction of H₂TBP (168 mg, 0.15 mmol), Eu(acac)₃·nH₂O (225 mg, 0.45 mmol) and ᵘPcLi₂ (170 mg) in 1,2,4-trichlorobenzene (30 mL) afforded three main bands upon column chromatography (silica, CHCl₃). The first band (brownish-red) was purified by SEC (THF). The resulting product was washed with methanol, affording a brown solid (4a, 67 mg, 36%): ¹H NMR (CDCl₃) δ 1.87 (s, 72H), 3.94 (s, 16H), 4.73 (d, J = 7.5 Hz, 8H), 6.68 (d, J = 6.6 Hz, 8H), 8.97 (m, 8H), 10.63 (br s, 8H), 11.40 (m, 8H), 12.73 (br s, 8H); LD-MS obsd 2482.3; FAB-MS obsd 2490.97, calcd exact mass 2490.96 (C₁₅₂H₁₃₆N₁₆Eu₂); λ_abs 354, 421, 492, 607 nm. The second band was purified by SEC (THF), affording a black solid (4b, 2.2 mg, 0.68%): ¹H NMR (CDCl₃) δ 2.91 (s, 36H), 8.03 (m, 16H), 9.58 (m, 16H), 9.99 (m, 8H), 12.19 (s, 8H), 13.43 (m, 8H); LD-MS obsd 2157.6; FAB-MS obsd 2166.65, calcd exact mass 2166.62 (C₁₂₄H₉₂N₂₀Eu₂); λ_abs 342, 406, 519, 652 nm. The third band (dark green) was further purified by column chromatography (silica, toluene), affording a green solid (4c, 34 mg, 11%): ¹H NMR (CDCl₃) δ 1.88 (s, 36H), 3.26 (s, 8H), 4.73 (d, J = 6.6 Hz, 4H), 6.62 (d, J = 7.2 Hz, 4H), 8.69 (m, 8H), 9.01 (m, 4H), 10.09 (m, 8H), 11.09 (m, 8H), 11.42 (m, 4H), 12.96 (br s, 8H); LD-MS obsd 2157.9; FAB-MS obsd 2166.61, calcd exact mass 2166.6 (C₁₂₄H₉₂N₂₀Eu₂); λ_abs 342, 419, 521, 619, 668, 721 nm.

Reaction of H₂PnP and ᵘPcLi₂ affording triple deckers 5a and 5c

The reaction of porphyrin H₂PnP (89 mg, 0.15 mmol), Eu(acac)₃·nH₂O (225 mg, 0.45 mmol) and ᵘPcLi₂ (170 mg) in 1,2,4-trichlorobenzene (30 mL) gave two main bands upon column chromatography (silica, CHCl₃). The first band (brownish-red) was purified by SEC (THF), affording a brown solid (5a, 59 mg, 39%): ¹H NMR (CDCl₃) δ 0.52 (br s, 16H), 0.66 (t, J = 6.9 Hz, 24H), 0.97–1.0 (m, 16H), 1.2–1.3 (m, 16H), 3.71 (m, 16H), 5.39 (s, 16H), 10.78 (br s, 8H), 12.69 (br s, 8H); LD-MS obsd 1987.5, 1931.6, 1917.2; FAB-MS obsd 1994.84, calcd exact mass 1994.83 (C₁₁₂H₁₂₀N₁₆Eu₂); λ_abs 347, 426, 500, 567, 620 nm. The second band was further purified by column chromatography (silica, toluene), affording a green solid (5c, 86 mg, 30%): ¹H NMR (CDCl₃) δ 0.40 (br s, 8H), 0.58

(t, $J = 6.9$ Hz, 12H), 0.85–0.93 (m, 8H), 1.02–1.06 (m, 8H), 2.87 (m, 8H), 4.53 (s, 8H), 8.78 (m, 8H), 10.23 (m, 8H), 11.13 (br s, 8H), 12.89 (br s, 8H); LD-MS obsd 1913.8, 1856.9; FAB-MS obsd 1918.56, calcd exact mass 1918.56 ($C_{104}H_{84}N_{20}Eu_2$); λ_{abs} 341, 406, 439, 522, 581, 624, 735 nm.

Reaction of H_2PnP and $(t\text{-}Bu)_4PcLi_2$ affording triple deckers 6a, 6c, and 6d

The reaction of H_2PnP (40 mg, 0.068 mmol), $Eu(acac)_3 \cdot nH_2O$ (103 mg, 0.21 mmol) and $(t\text{-}Bu)_4PcLi_2$ (58 mg) in 1,2,4-trichlorobenzene (16 mL) gave three main bands after column chromatography (silica, CHCl₃). The first band was further purified by SEC (THF). The first band (greenish-brown) from the SEC column was further purified by column chromatography (silica, hexanes–ethyl acetate from 9:1 to 7:3), affording a brown solid (6a, 29 mg, 39%): ¹H NMR (CDCl₃) 0.6–0.8 (m, 40H), 1.19 (m, 16H), 1.45 (m, 16H), 3.52 (s, 36H), 3.7–4.0 (m, 16H), 5.0–5.3 (m, 16H), 10.6–10.9 (m, 4H), 12.0–12.5 (m, 8H); LD-MS obsd 2218.8, 2162.0, 2149.0; FAB-MS obsd 2217.97, calcd exact mass 2218.07 ($C_{128}H_{152}N_{16}Eu_2$); Anal. Calcd: C, 69.30; H, 6.91; N, 10.10. Found: C, 69.04; H, 6.86; N, 9.82%; λ_{abs} 357, 427, 502, 566, 626 nm. The third band was further purified by column chromatography (silica, toluene), giving two bands, of which the first band (dark green) was finally purified by another column chromatography (silica, hexanes–ethyl acetate from 9:1 to 7:3), affording a black solid (6c, 17 mg, 11%): The ¹H NMR (CDCl₃) spectrum was collected but the mixture of regioisomers prevented interpretation. LD-MS obsd 2374.0; FAB-MS obsd 2366.11, calcd exact mass 2366.05 ($C_{136}H_{147}N_{20}Eu_2$); λ_{abs} 345, 413, 527, 583, 629, 736 nm. The second band from the second silica column was further purified by column chromatography (silica, hexanes–ethyl acetate from 9:1 to 7:3), affording a black solid (6d, 11 mg, 17% based on the starting phthalocyanine): The ¹H NMR spectrum (CDCl₃) was collected but the mixture of regioisomers prevented interpretation. LD-MS obsd 2523.1; FAB-MS obsd 2514.96, calcd exact mass 2515.04 ($C_{144}H_{144}N_{24}Eu_2$); λ_{abs} 341, 649 nm.

Reaction of H_2PnP and $(Me)_8PcLi_2$ affording triple deckers 7a and 7c

The reaction of H_2PnP (50 mg, 0.085 mmol), $Eu(acac)_3 \cdot nH_2O$ (130 mg, 0.26 mmol) and $(Me)_8PcLi_2$ (250 mg) in 1,2,4-trichlorobenzene (20 mL) gave two main bands after column chromatography (silica, CHCl₃). The first band (brownish-red) was further purified by SEC (THF), followed by column chromatography [silica, hexanes–toluene (1:1) slowly enriched to 100% toluene] and another chromatography (silica, hexanes–CH₂Cl₂ from 9:1 to 4:1), affording a brown solid (7a, 7 mg, 8%): ¹H NMR (CDCl₃) δ 0.6–0.8 (m, 16H), 0.90 (t, $J = 6.9$ Hz, 24H), 1.2–1.5 (m, 32H), 3.8–3.9 (m, 16H), 4.24 (s, 24H), 5.41 (s, 16H), 12.27 (s, 8H); LD-MS obsd 2109.2, 2051.5, 2037.6; FAB-MS obsd 2106.98, calcd exact mass 2106.96 ($C_{120}H_{136}N_{16}Eu_2$); λ_{abs} 362, 428, 502, 567, 625 nm. The second band (greenish-black) was further purified by column chromatography (silica, toluene) followed by another chromatography (silica, CH₂Cl₂), affording a black solid (7c, 3 mg, 2%): The ¹H NMR (CDCl₃) spectrum was collected, but the amount of material was insufficient to obtain a good spectrum. LD-MS obsd 2143.3, 1401.7; FAB-MS obsd 2142.79, calcd exact mass 2142.81 ($C_{120}H_{116}N_{20}Eu_2$); λ_{abs} 351, 417, 631, 652, 684 nm. Both 7a and 7c slowly decomposed during purification.

Reaction of H_2TPP and $(Me)_8PcLi_2$ affording triple deckers 8a and 8c

The reaction of H_2TPP (83 mg, 0.14 mmol), $Eu(acac)_3 \cdot nH_2O$ (205 mg, 0.41 mmol) and $(Me)_8PcLi_2$ (380 mg) in 1,2,4-trichlorobenzene (30 mL) gave three bands upon column

chromatography (silica, CHCl₃). The first band was further purified by SEC (THF), affording a greenish-brown solid. Final purification was achieved by chromatography (silica, toluene) followed by washing the product with hexanes (8a, 20 mg, 14%): ¹H NMR (CDCl₃) δ 3.9–4.2 (m, 40H), 4.88 (d, $J = 7.2$ Hz, 8H), 6.79 (t, $J = 7.2$ Hz, 8H), 8.13 (t, $J = 8.1$ Hz, 8H), 9.07 (t, $J = 6.9$ Hz, 8H), 11.6–11.7 (m, 8H), 12.2–12.6 (m, 8H); LD-MS obsd 2160.3, 1393.4, 767.3; FAB-MS obsd 2154.58, calcd exact mass 2154.58 ($C_{128}H_{88}N_{16}Eu_2$); λ_{abs} 364, 420, 496, 608 nm. The third band (greenish-black) was purified twice more by column chromatography (silica, toluene; silica, CH₂Cl₂). The compound thus obtained was finally purified by SEC (THF), affording a black solid after washing with hexanes (8c, 27 mg, 8.9%): ¹H NMR (CDCl₃) δ 3.89 (s, 8H), 4.28 (m, 24H), 4.4–4.5 (m, 4H), 4.54 (m, 24H), 6.43 (t, $J = 6.9$ Hz, 4H), 7.73 (t, $J = 7.5$ Hz, 4H), 8.28 (m, 4H), 9.12 (br s, 4H), 9.41 (m, 8H), 12.63 (m, 8H); LD-MS obsd 2173.5, 1406.3; FAB-MS obsd 2166.61, calcd exact mass 2166.62 ($C_{124}H_{92}N_{20}Eu_2$); λ_{abs} 352, 416, 535, 625, 740 nm.

Reaction of H_2OEP and $(Me)_8PcLi_2$ affording triple decker 9a

The reaction of H_2OEP (82 mg, 0.15 mmol), $Eu(acac)_3 \cdot nH_2O$ (235 mg, 0.47 mmol) and $(Me)_8PcLi_2$ (430 mg) in 1,2,4-trichlorobenzene (35 mL) gave one very polar main band after column chromatography (silica, CHCl₃ slowly enriched with up to 10% methanol). The band was further purified by chromatography (silica, toluene–Et₃N, from 1% to 2% Et₃N) followed by washing with hexanes, affording a brown solid (9a, 32 mg, 20% yield; 90% purity): LD-MS obsd 1995.83, calcd avg mass 1994.21 ($C_{112}H_{120}N_{16}Eu_2$); λ_{abs} 353, 404, 484, 594 nm.

Reaction of H_2OEP and $(heptyl)_8PcLi_2$ affording triple decker 10b

The reaction of H_2OEP (14 mg, 0.026 mmol), $Eu(acac)_3 \cdot nH_2O$ (38 mg, 0.076 mmol) and $(heptyl)_8PcLi_2$ (50 mg) in 1,2,4-trichlorobenzene (6 mL) gave a green solid after column chromatography (silica, CHCl₃). The solid was dissolved in toluene and purified by SEC (toluene). Two bands were obtained, of which the second band was further purified by chromatography (silica, hexanes–toluene from 3:1 to 1:1), affording a green solid (10b, 16 mg, 18%): ¹H NMR (CDCl₃) δ 1.37 (t, $J = 5.7$ Hz, 48H), 1.8–2.0 (m, 64H), 2.12 (m, 32H), 2.32 (m, 32H), 2.6–2.8 (m, 32H), 3.82 (s, 32H), 5.15 (m, 24H), 5.39 (s, 16H), 9.18 (s, 16H), 15.63 (br s, 4H); LD-MS obsd 3437.4; FAB-MS obsd 3432.10, calcd exact mass 3432.25 ($C_{212}H_{300}N_{20}Eu_2$); λ_{abs} 344, 444, 504, 625, 658 nm.

Reaction of H_2PnP and $NcLi_2$ affording triple decker 11a

The reaction of H_2PnP (66 mg, 0.11 mmol), $Eu(acac)_3 \cdot nH_2O$ (140 mg, 0.28 mmol) and $NcLi_2$ (100 mg) in 1,2,4-trichloro-benzene (21 mL) gave four bands upon column chromatography (silica, CHCl₃). The first band was further purified by SEC (THF). Final purification by chromatography [silica, hexanes–CH₂Cl₂ (3:1)] afforded a green solid (11a, 4 mg, 3%): LD-MS obsd 2203.5, 2146.9, 2132.9; FAB-MS obsd 2194.89, calcd exact mass 2194.89 ($C_{128}H_{128}N_{16}Eu_2$); λ_{abs} 330, 429, 543, 612 nm.

4-(3-Methyl-3-hydroxybut-1-yn-1-yl)benzaldehyde (14)

Following a standard procedure,[21,25] samples of 4-bromo-benzaldehyde (3.0 g, 16 mmol), $Pd(PPh_3)_2Cl_2$ (110 mg, 0.170 mmol) and CuI (16 mg, 0.084 mmol) were placed in a Schlenk flask. The flask was then evacuated and purged with argon (3 times) on the Schlenk line. Freshly distilled and degassed TEA (32 mL) was added. After purging with argon, 2-methylbut-3-yn-2-ol (1.90 mL, 19.4 mmol) was added. The reaction mixture was stirred for 2 h at 40 °C. The progress of

the reaction was monitored by GC-MS. Column chromatography (silica, CH_2Cl_2) of the crude reaction mixture followed by bulb-to-bulb distillation (93–95 °C, 0.001 mmHg) afforded a pale yellow oil (2.9 g, 95%): ^{1}H NMR (CDCl$_3$) δ 1.61 (s, 6H), 2.23 (br s, 1H), 7.52 (AB/2, $J = 8.1$ Hz, 2H), 7.79 (AB/2, $J = 8.1$ Hz, 2H), 9.02 (s, 1H); ^{13}C NMR δ 31.9, 66.1, 81.9, 98.8, 129.8, 130.1, 132.7, 135.9, 192.3; IR (film) v (cm^{-1}) 790.4, 830.1, 906.3, 963.4, 1014.3, 1046.1, 1165.9, 1207.0, 1273.4, 1303.0, 1373.0, 1457.6, 1563.8, 1603.6, 1700.0, 2228.1, 2735.0, 2837.8, 2934.1, 2982.2, 3413.3; MS (EI) m/z 188 (M$^+$, 35%), 173 (100%), 159 (10%); EI-MS obsd 188.0835, calcd exact mass 188.0837 ($C_{12}H_{12}O_2$).

5-[4-(3-Methyl-3-hydroxybut-1-yn-1-yl)phenyl]dipyrromethane (15)

Following a standard procedure,[22] a solution of 14 (2.5 g, 13 mmol) in pyrrole (23.0 mL, 330 mmol) was treated with TFA (72 µL, 1.3 mmol). After 5 min, the reaction was quenched with 0.1 M NaOH. The mixture was extracted with ethyl acetate. The ethyl acetate layer was washed with water, dried, and concentrated under vacuum, affording an oil. Unlike in the standard procedure,[22] Kugelrohr distillation was not performed. Column chromatography (silica, CH_2Cl_2 slowly enriched with up to 7.5% methanol) of the oil followed by crystallization from ethanol–water afforded white crystals (2.3 g, 56%): mp 145–146 °C; ^{1}H NMR (CDCl$_3$) δ 1.62 (s, 6H), 1.89 (br s, 1H), 5.46 (s, 1H), 5.89 (s, 2H), 6.17 (dd, $J = 5.7$, 3.0 Hz, 2H), 6.71 (m, 2H), 7.1–7.2 (m, 2H), 7.3–7.4 (m, 2H), 7.97 (br s, 2H); ^{13}C NMR δ 32.2, 44.4, 66.3, 82.7, 94.5, 108.1, 109.1, 118.2, 122.0, 129.1, 132.5, 132.8, 143.1; Anal. Calcd for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62; N, 9.20. Found: C, 79.03; H, 6.69; N, 9.29%.

5-[4-(3-Methyl-3-hydroxybut-1-yn-1-yl)phenyl]-10,15,20-tri-*n*-pentylporphyrin (17)

Following a standard procedure,[17] a solution of dipyrromethane 15 (530 mg, 1.74 mmol) and dipyrromethane-dicarbinol 16 [prepared directly from the diacyldipyrromethane (720 mg, 1.8 mmol)][17] in CH_3CN (700 mL) was treated with TFA (1.6 mL, 29 mmol). After 4 min, DDQ (1.2 g, 5.3 mmol) was added and the reaction mixture was stirred for 1 h. Column chromatography [silica, toluene–CH_2Cl_2 (3:2)] afforded a purple solid (275 mg, 23%): ^{1}H NMR (CDCl$_3$) δ −2.68 (br s, 2H), 0.9–1.1 (m, 9H), 1.5–1.6 (m, 6H), 1.7–1.9 (m, 12H), 2.2–2.3 (br s, 1H), 2.4–2.6 (m, 6H), 4.8–5.0 (m, 6H), 7.84 (d, $J = 8.1$ Hz, 2H), 8.14 (d, $J = 7.8$ Hz, 2H), 8.78 (d, $J = 5.1$ Hz, 2H), 9.37 (d, $J = 5.1$ Hz, 2H), 9.49 (dd, $J = 9.6$, 5.1 Hz, 4H); LD-MS obsd 680.6, 623.1; FAB-MS obsd 678.4310, calcd exact mass 678.4298 ($C_{46}H_{54}N_4O$); λ_{abs} (CH$_2$Cl$_2$) 422, 520, 554, 600, 658 nm; λ_{em} (λ_{exc} 520 nm) 661, 731 nm.

5-(4-Ethynylphenyl)-10,15,20-tri-*n*-pentylporphyrin (18)

Following a standard procedure,[21] porphyrin 17 (50 mg, 0.074 mmol) was dissolved in toluene (5 mL), then powdered NaOH (100 mg, 2.5 mmol) was added. The reaction mixture was refluxed for 2 h. After cooling to room temperature, the mixture was purified by column chromatography [silica, CH_2Cl_2–hexanes (3:2)], affording a purple solid (41 mg, 90%): ^{1}H NMR (CDCl$_3$) δ −2.67 (s, 2H), 1.0–1.1 (m, 9H), 1.5–1.7 (m, 6H), 1.7–1.9 (m, 6H), 2.4–2.6 (m, 6H), 3.37 (s, 1H), 4.8–5.0 (m, 6H), 7.91 (d, $J = 7.2$ Hz, 2H), 8.15 (d, $J = 8.1$ Hz, 2H), 8.80 (d, $J = 5.1$ Hz, 2H), 9.37 (d, $J = 4.5$ Hz, 2H), 9.47 (dd, $J = 8.1$, 4.2 Hz, 4H); LD-MS obsd 622.2, 564.8; FAB-MS obsd 620.3886, calcd exact mass 620.3879 ($C_{43}H_{48}N_4$); λ_{abs} (CH$_2$Cl$_2$) 420, 519, 555, 597, 657 nm; λ_{em} (λ_{exc} 535 nm) 659, 728 nm.

5-(6-Bromohexyl)dipyrromethane (19)

Following a standard procedure,[22] 6-bromoheptanal (9.7 mmol, used directly from the PCC oxidation of 6-bromoheptanol)[23] was reacted with pyrrole (17 mL) in the presence of TFA (52 µL, 0.94 mmol). After 5 min, the same workup procedure as used for compound 15 was performed. Column chromatography (silica, toluene) afforded a colorless oil (1.2 g, 41%): ^{1}H NMR (toluene-d$_8$) δ 1.0–1.2 (m, 6H), 1.48 (m, 2H), 1.7–1.8 (m, 2H), 2.95 (t, $J = 7.1$ Hz, 2H), 3.61 (t, $J = 7.6$ Hz, 1H), 6.05 (s, 2H), 6.21 (m, 2H), 6.27 (m, 2H), 6.89 (br s, 2H); ^{13}C NMR δ 28.0, 28.7, 29.3, 33.4, 33.8, 35.0, 38.1, 106.3, 108.5, 117.6, 133.8; Anal. Calcd for $C_{15}H_{21}BrN_2$, C, 58.26; H, 6.85; N, 9.06; Br, 25.84. Found: C, 58.41; H, 6.95; N, 9.00; Br, 25.76%; FAB-MS obsd 308.0910, calcd exact mass 308.0888.

5-(6-Bromohexyl)-10,15,20-tri-*n*-pentylporphyrin (20)

Following a standard procedure,[17] a solution of dipyrromethane 19 (620 mg, 2.0 mmol) and dipyrromethane-dicarbinol 16 [prepared directly from the diacyldipyrromethane (820 mg, 2.0 mmol)][17] in CH_3CN (800 mL) at room temperature was treated with TFA (1.9 mL, 34 mmol). After 4 min, DDQ (1.4 g, 5.4 mmol) was added and the reaction mixture was stirred for 1 h. Column chromatography [silica, hexanes–CH_2Cl_2 (2:1)] followed by a second column [alumina, hexanes–CH_2Cl_2 (3:2)] gave a purple solid (460 mg, 34%): ^{1}H NMR (CDCl$_3$) δ −2.59 (br s, 2H), 1.21 (m, 9H), 1.5–1.8 (m, 10H), 1.9–2.0 (m, 8H), 2.47 (m, 2H), 2.66 (m, 6H), 3.46 (t, $J = 7.1$ Hz, 2H), 4.74 (t, $J = 7.7$ Hz, 2H), 4.91 (t, $J = 7.7$ Hz, 6H), 9.34 (AB/2, $J = 4.5$ Hz, 2H), 9.45 (AB/2, $J = 5.1$ Hz, 2H), 9.47 (br s, 4H); LD-MS obsd 684.7, 626.8, 604.9, 576.8, 549.1, 533.2; FAB-MS obsd 682.3605, calcd exact mass 682.3610 ($C_{41}H_{55}BrN_4$); λ_{abs} (toluene) 400, 418, 521, 555, 602, 658 nm; λ_{em} (λ_{exc} 550 nm) 611, 734 nm.

5-(6-Thiocyanatohexyl)-10,15,20-tri-*n*-pentylporphyrin (21)

A solution of 20 (50 mg, 0.073 mmol) in DMF (5 mL) was treated with KSCN (40 mg, 0.40 mmol) and the resulting mixture was stirred at 60 °C for 20 h. The reaction mixture was then diluted with water, extracted with diethyl ether and dried (Na$_2$SO$_4$). Column chromatography (alumina, hexanes–CH_2Cl_2 from 3:2 to 1:1) afforded a purple solid (46 mg, 99%): ^{1}H NMR (CDCl$_3$) δ −2.65 (br s, 2H), 1.0–1.1 (m, 9H), 1.4–1.5 (m, 2H), 1.5–1.7 (m, 10H), 1.7–1.9 (m, 6H), 2.40 (m, 2H), 2.5–2.6 (m, 6H), 2.70 (t, $J = 7.4$ Hz, 2H), 4.80 (t, $J = 8.1$ Hz, 2H), 4.92 (m, 6H), 9.35 (AB/2, $J = 5.4$ Hz, 2H), 9.4–9.5 (m, 6H); LD-MS obsd 2480.8, 1907.9, 1875.7, 1850.3, 1816.0, 1804.0, 1269.7, 1244.1, 1211.0, 1200.1, 663.8 (M$^+$), 636.5, 604.5, 576.3, 534.1; FAB-MS obsd 661.4164, calcd exact mass 661.4178 ($C_{42}H_{55}N_5S$); λ_{abs} (toluene) 421, 521, 554, 605, 662 nm; λ_{em} (λ_{exc} 555 nm) 663, 739 nm.

Preparation of triple-decker building blocks 22a and 22c

The reaction of porphyrin 18 (35 mg, 0.057 mmol), Eu(acac)$_3$·nH$_2$O (88 mg, 0.17 mmol) and (*t*-Bu)$_4$PcLi$_2$ (49 mg) in 1,2,4-trichlorobenzene (13 mL) resulted in three bands after column chromatography (silica, CHCl$_3$). The first band was further purified by SEC (THF), affording a greenish-black solid (22a, 14 mg, 22%): ^{1}H NMR (CDCl$_3$) δ 0.85 (br s, 4H), 0.34 (t, $J = 6.9$ Hz, 6H), 0.5–1.0 (m, 28H), 1.25 (m, 8H), 1.57 (m, 8H), 2.6 (br s, 4H), 3.47 (m, 38H), 3.57 (s, 2H), 4.28 (br s, 8H), 4.4–4.6 (m, 4H), 4.7–4.9 (m, 6H), 5.1–5.2 (m, 4H), 5.9–6.1 (m, 4H), 6.81 (d, $J = 6.6$ Hz, 2H), 8.76 (d, $J = 6.6$ Hz, 2H), 9.66 (d, $J = 5.7$ Hz, 2H), 10.96 (m, 4H), 12.68 (m, 8H); LD-MS obsd 2284.9, 2227.2, 2215.8; FAB-MS obsd 2278.99, calcd exact mass 2278.99 ($C_{134}H_{140}N_{16}Eu_2$); λ_{abs} 358, 428, 502, 566, 619 nm. The third band (dark green) was further purified by

column chromatography (silica, toluene), affording a dark green solid (**22c**, 16 mg, 12%): The ^{1}H NMR spectrum (CDCl$_3$) was collected but the mixture of regioisomers prevented interpretation. LD-MS obsd 2403.5; FAB-MS obsd 2396.96, calcd exact mass 2397.02 (C$_{139}$H$_{142}$N$_{20}$Eu$_2$); λ_{abs} 345, 419, 530, 583, 627, 733 nm.

Preparation of triple-decker building blocks 23a and 23c

The reaction of porphyrin **12** (100 mg, 0.14 mmol), Eu-(acac)$_3$·nH$_2$O (213 mg, 0.42 mmol) and (t-Bu)$_4$PcLi$_2$ (120 mg) in 1,2,4-trichlorobenzene (32 mL) resulted in three bands upon column chromatography (silica, CHCl$_3$). The first band was further purified by SEC (THF), affording a brownish solid (**23a**, 28 mg, 16%): ^{1}H NMR (CDCl$_3$) δ −0.81 (br s, 4H), 0.38 (t, J = 6.9 Hz, 6H), 0.5–1.0 (m, 24H), 1.1–1.3 (m, 8H), 1.5–1.7 (m, 8H), 2.05 (s, 4H), 2.6–2.7 (m, 4H), 3.4–3.5 (m, 36H), 4.2–4.4 (m, 8H), 4.4–4.7 (m, 4H), 4.7–5.0 (m, 6H), 5.1–5.3 (m, 4H), 5.9–6.2 (m, 4H), 7.05 (d, J = 7.5 Hz, 2H), 9.01 (d, J = 6.6 Hz, 2H), 9.50 (d, J = 6.0 Hz, 2H), 10.9–11.1 (m, 4H), 12.6–12.9 (m, 8H); LD-MS (with POPOP as a matrix) obsd 2491.0, 2442.3, 2434.2, 2363.7; FAB-MS obsd 2482.78, calcd exact mass 2482.78 (C$_{130}$H$_{138}$N$_{16}$I$_2$Eu$_2$); λ_{abs} 359, 428, 501, 569, 619 nm. The third band (dark green) was further purified by chromatography (silica, toluene), affording a dark green solid (**23c**, 40 mg, 12%): The ^{1}H NMR spectrum (CDCl$_3$) was collected but the mixture of regioisomers prevented interpretation. LD-MS obsd 2508.2, 2381.7; FAB-MS obsd 2498.92, calcd exact mass 2498.91 (C$_{137}$H$_{141}$N$_{20}$IEu$_2$); λ_{abs} 345, 416, 529, 583, 627, 732 nm.

Preparation of triple-decker building blocks 24a, 24b, and 24c

The reaction of porphyrin **13** (88 mg, 0.10 mmol), Eu(acac)$_3$·nH$_2$O (150 mg, 0.30 mmol) and ^{u}PcLi$_2$ (114 mg) in 1,2,4-trichlorobenzene (20 mL) resulted in four bands upon column chromatography (silica, CHCl$_3$). The first band (olive-brown) was purified by SEC (THF). The first band (greenish-brown) was collected. Removal of the solvent and washing the product with methanol afforded a greenish-black solid (**24a**, 34 mg, 26%): ^{1}H NMR (CDCl$_3$) δ 0.62 (s, 18H), 1.89 (s, 54H), 3.83–4.03 (m, 16H), 4.76 (m, 9H), 6.71 (m, 6H), 6.84 (m, 2H), 9.00 (br s, 6H), 9.19 (m, 2H), 10.65 (br s, 8H), 11.46–11.60 (m, 8H), 12.73 (br s, 8H); LD-MS obsd 2574.1; FAB-MS obsd 2570.90, calcd exact mass 2570.91 (C$_{154}$H$_{136}$N$_{16}$Si$_2$Eu$_2$); λ_{abs} 355, 421, 493, 559, 606 nm. The third band (black) was purified by SEC (THF). The second band (black) from the SEC column was collected. Removal of the solvent and washing the product with methanol afforded a black solid (**24b**, 3.5 mg, 1.6%): ^{1}H NMR (CDCl$_3$) δ 0.85 (s, 18H), 2.89, 2.94 (m, 26H), 8.05 (br s, 16H), 9.59 (br s, 16H), 9.99 (m, 2H), 10.10 (m, 4H), 11.98–12.20 (m, 4H), 13.52 (m, 2H), 13.68 (m, 4H); LD-MS obsd 2209.1, 2206.2; FAB-MS obsd 2206.60, calcd exact mass 2206.60 (C$_{125}$H$_{92}$N$_{20}$SiEu$_2$); λ_{abs} 343, 416, 519, 625, 653 nm. The last band (green) was further purified by chromatography (silica, toluene). The first band was collected. Removal of the solvent and washing the product with methanol afforded a green solid (**24c**, 20 mg, 9.1%): ^{1}H NMR (CDCl$_3$) δ 0.68 (s, 9H), 1.86 (m, 27H), 3.20–3.29 (m, 8H), 4.71–4.91 (m, 4H), 6.67 (m, 3H), 6.91 (m, 1H), 8.72 (br s, 8H), 9.08–9.16 (m, 3H), 9.41 (m, 1H), 10.10 (br s, 8H), 11.10 (br s, 8H), 11.69 (m, 2H), 11.88 (m, 1H), 12.16 (m, 1H), 12.97 (br s, 8H); LD-MS obsd 2217.1 (M$^+$), 1181.4 [M$^+$−(Por)Eu], 919.3 [M$^+$−(^{u}Pc)Eu(^{u}Pc)]; FAB-MS obsd 2206.60, calcd exact mass 2206.60 (C$_{125}$H$_{92}$N$_{20}$SiEu$_2$); λ_{abs} 342, 417, 522, 552, 618, 721 nm.

Triple-decker building block 25

A sample of ethynyl triple decker **24c** (20 mg, 9.1 μmol) was treated with K$_2$CO$_3$ (15 mg, 0.11 mmol) and worked-up following the standard procedure.[24] Column chromatography (silica, CHCl$_3$) afforded a black solid (18 mg, 94%): ^{1}H NMR (CDCl$_3$) δ 1.96 (m, 27H), 3.30–3.38 (m, 8H), 3.71 (s, 1H), 4.77 (d, J = 7.2 Hz, 3H), 5.00 (d, J = 6.6 Hz, 1H), 6.70 (m, 3H), 6.95 (d, J = 7.2 Hz, 1H), 8.76 (br s, 8H), 9.09–9.16 (m, 3H), 9.40 (m, 1H), 10.16 (br s, 8H), 11.17 (br s, 8H), 11.56 (m, 2H), 11.73 (m, 1H), 12.00 (m, 1H), 13.04 (br s, 8H); LD-MS obsd 2136.5; FAB-MS obsd 2134.56, calcd exact mass 2134.56 (C$_{122}$H$_{84}$N$_{20}$Eu$_2$); λ_{abs} 343, 415, 522, 552, 618, 722 nm.

S-(Acetylthio)-derivatized triple decker TD3

Route 1: Samples of ethynyl triple decker **22c** (39 mg, 16 μmol), 1-(S-acetylthio)-4-iodobenzene[2] (44.5 mg, 0.16 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (1.7 mg, 2.4 μmol) and CuI (0.22 mg, 1.1 μmol) were added to a Schlenk flask. The flask was evacuated and purged with argon three times. Then deaerated THF (6.0 mL) and deaerated DIEA (1.5 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–Et$_2$O (60 : 1)] and LD-MS. After 20 h, the solvent was removed under vacuum and the residue was chromatographed (silica, toluene). Elution with toluene and then toluene–ether (60 : 1) did not afford separation of products. The residue was chromatographed (SEC, THF), affording the butadiyne-linked dyad **26** as the first band [LD-MS obsd 4788.3, calcd avg mass 4791.4 (C$_{278}$H$_{282}$N$_{40}$Eu$_4$)]. The second band contained the title compound together with acetylated starting material **27** [LD-MS obsd 2440.3, calcd avg mass 2438.8 (C$_{141}$H$_{144}$N$_{20}$OEu$_2$)]. These two products were not separable by any chromatographic method examined.

Route 2: Samples of iodo triple decker **23c** (35 mg, 14 μmol), 1-(S-acetylthio)-4-ethynylbenzene[28] (3 mg, 14 μmol), Pd$_2$(dba)$_3$ (2.0 mg, 22 μmol) and P(o-tol)$_3$ (5.1 mg, 17 μmol) were added to a Schlenk flask. The flask was evacuated and purged with argon three times. Then deaerated toluene (4.6 mL) and deaerated DIEA (0.9 mL) were added by syringe. The flask was immersed in an oil bath at 35 °C and stirred under argon. The reaction was monitored by TLC (silica, toluene) and LD-MS. After 44 h, the solvent was removed under vacuum. The residue was chromatographed (silica, toluene). The first band contained the desired product together with a trace of unreacted starting material. Further purification by a second column chromatography procedure (silica, toluene) afforded the title compound as a black solid (5.0 mg, 14%): A ^{1}H NMR spectrum (CDCl$_3$) was collected but the mixture of regio-isomers prevented interpretation. LD-MS obsd 2550.3, 2507.8, 2495.2, 2480.2; FAB-MS obsd 2547.05, calcd exact mass 2547.03 (C$_{147}$H$_{148}$N$_{20}$OSEu$_2$); λ_{abs} 339, 415, 527, 577, 625, 723 nm.

S-(Acetylthio)-derivatized triple decker TD4

Samples of ethynyl triple decker **25** (15 mg, 7.0 μmol), 1-(S-acetylthio)-4-iodobenzene[2] (2.0 mg, 7.0 μmol), Pd$_2$(dba)$_3$ (1.0 mg, 1.1 μmol) and P(o-tol)$_3$ (2.5 mg, 8.3 μmol) were added to a Schlenk flask. The flask was evacuated and purged with argon three times. Then deaerated toluene (3 mL) and deaerated DIEA (0.6 mL) were added by syringe. The flask was immersed in an oil bath at 35 °C and stirred under argon. The reaction was monitored by TLC (silica, toluene) and LD-MS. After 24 h, the solvent was removed under vacuum. The residue was chromatographed [silica, toluene–ether (60 : 1)]. The first band contained the desired product together with traces of unreacted starting material. Further purification by chromatography (silica, toluene) afforded a dark band. Evaporation of the solvent and washing the product with methanol afforded a black solid (3.1 mg, 19%): ^{1}H NMR (CDCl$_3$) δ 1.91 (m, 27H), 2.62 (s, 3H), 3.28 (m, 8H), 4.70–4.80 (m, 3H), 4.98 (d, J = 6.6 Hz, 1H), 6.68 (m, 4H), 6.94 (d, J = 6.6 Hz, 1H), 7.54 (m, 1H), 7.71 (m, 1H), 8.03 (m, 1H), 8.71 (br s, 8H), 9.05–9.12 (m, 3H), 9.42 (m, 1H), 10.10 (br s, 8H),

11.11 (br s, 8H), 11.56 (m, 2H), 11.72 (m, 1H), 12.02 (m, 1H), 12.98 (br s, 8H); LD-MS obsd 2291.4 (M$^+$), 2250.2 (M$^+$−CH$_3$CO), 1181.0 [M$^+$−(Por)Eu], 1111.6 [M$^+$−(^{u}Pc)-Eu(^{u}Pc)], 1067.8 [(^{u}Pc)Eu(^{u}Pc)−CH$_3$CO]; FAB-MS obsd 2284.59, calcd exact mass 2284.58 (C$_{130}$H$_{90}$OSN$_{20}$Eu$_2$); λ_{abs} 341, 419, 523, 618, 721 nm.

Triple-decker building block 29c

The reaction of porphyrin **20** (50 mg, 0.073 mmol), Eu(acac)$_3$ · nH$_2$O (110 mg, 0.22 mmol) and ^{u}PcLi$_2$ (83 mg) in 1,2,4-trichlorobenzene (17 mL) resulted in two bands after column chromatography (silica, CHCl$_3$). The second band (green) was further purified by column chromatography (silica, toluene), affording the desired triple decker along with some impurities. Final purification by preparative TLC [silica, toluene–CH$_2$Cl$_2$ (4 : 1)] afforded a green solid (10 mg, 11%): ^{1}H NMR (CDCl$_3$) δ 0.41 (m, 8H), 0.57 (t, J=6.9 Hz, 9H), 0.8–1.1 (m, 16H), 1.4–1.5 (m, 2H), 2.8–3.0 (m, 8H), 3.17 (t, J=6.6 Hz, 2H), 4.54 (br s, 8H), 8.75 (m, 8H), 10.18 (s, 8H), 11.10 (s, 8H), 12.86 (s, 8H); LD-MS (POPOP) obsd 2009.6, 1964.8, 1929.2, 1176.0, 672.0; FAB-MS obsd 2010.49, calcd exact mass 2010.49 (C$_{105}$H$_{85}$BrN$_{20}$Eu$_2$); λ_{abs} 341, 407, 439, 522, 581, 624, 736 nm.

S-(Acetylthio)-derivatized triple decker TD5

A solution of **29c** (9 mg, 0.005 mmol) in THF (2 mL) was treated with KSAc (10 mg, 0.088 mmol) and 18-crown-6 (24 mg, 0.091 mmol) following a known procedure.[31] The resulting mixture was stirred for 5 h at room temperature. Then the mixture was diluted with water and extracted with diethyl ether and CH$_2$Cl$_2$. The organic layers were combined, concentrated, and chromatographed (silica, toluene), affording a dark green solid (5 mg, 50%): ^{1}H NMR (CDCl$_3$) δ 0.3–0.5 (m, 8H), 0.55 (t, J=7.1 Hz, 9H), 0.8–1.1 (m, 16H), 1.2–1.3 (m, 2H), 2.29 (s, 3H), 2.65 (t, J=7.4 Hz, 2H), 2.84 (m, 8H), 4.49 (br s, 8H), 8.72 (s, 8H), 10.13 (s, 8H), 11.06 (s, 8H), 12.81 (s, 8H); LD-MS (POPOP) obsd 2040.6 (M+32)$^+$, 2008.4 (M)$^+$, 1965.3, 1933.1, 1863.1, 1178.7, 830.2, 673.6; LD-MS 2008.4, 2040.6 [4.4 : 1 ratio of M$^+$: (M+32)$^+$ peaks]; FAB-MS obsd 2006.58, calcd exact mass 2006.56 (C$_{107}$H$_{88}$N$_{20}$SOEu$_2$); λ_{abs} 341, 408, 440, 523, 583, 624, 740 nm. A larger-scale preparation afforded 15 mg (50%); identical spectroscopic data were observed except a 2.4 : 1 ratio of the M : (M+32) peaks was observed upon LD-MS analysis. This latter material was used for electrochemical examination as reported herein.

Thiocyanate-derivatized triple decker TDSCN

Reaction of porphyrin **21** (48 mg, 0.072 mmol), Eu-(acac)$_3$·nH$_2$O (110 mg, 0.22 mmol) and ^{u}PcLi$_2$ (83 mg) in 1,2,4-trichlorobenzene (17 mL) resulted in three bands upon column chromatography (silica, CHCl$_3$). The last band (green) was further purified [SEC, THF; silica, toluene–diethyl ether (200 : 1)], affording a green solid (8 mg, 6%): ^{1}H NMR (CDCl$_3$) δ 0.3–0.5 (br s, 8H), 0.55 (t, J=7.4 Hz, 9H), 0.7–0.9 (m, 8H), 0.9–1.1 (m, 8H), 1.3–1.4 (m, 2H), 2.47 (t, J=7.4 Hz, 2H), 2.88 (m, 8H), 4.4–4.6 (m, 8H), 8.71 (s, 8H), 10.12 (m, 1H), 11.08 (m, 1H), 12.84 (br s, 8H); LD-MS (POPOP) obsd 1988.7, 1963.7, 1929.8, 812.0, 672.7; FAB-MS obsd 1989.56, calcd exact mass 1989.56 (C$_{105}$H$_{85}$N$_{21}$SEu$_2$); λ_{abs} 340, 406, 440, 524, 581, 624, 733 nm.

Electrochemical studies

The solution electrochemical studies were performed using techniques and instrumentation previously described.[39] For triple deckers **1a**, **2**, **3**, **6** and **7**, the solvent was BuCN; for triple deckers **1c**, **4**, **5** and **8–11**, the solvent was CH$_2$Cl$_2$. For all complexes, 0.1 M Bu$_4$NPF$_6$ (Aldrich, recrystallized three times from methanol and dried under vacuum at 110 °C) served as

supporting electrolyte. The potentials were measured *vs.* Ag/Ag$^+$; $E\frac{1}{2}$(FeCp$_2$/FeCp$_2^+$)=0.19 V.

The SAM electrochemical studies were performed using a 10 μm diameter Au ball working electrode. This electrode was prepared as previously described.[34,40] The SAMs were formed by placing the electrode in a 2 mg mL^{-1} solution of the triple decker for 20 min and sonicating for an additional 1 min. The electrode was then removed from the sample solution and rinsed with distilled CH$_2$Cl$_2$. For all of the SAMs, the measurements were performed in dried, distilled CH$_2$Cl$_2$ containing 0.1 M Bu$_4$NPF$_6$. The potentials were measured *vs.* Ag/Ag$^+$; $E\frac{1}{2}$(FeCp$_2$/FeCp$_2^+$)=0.19 V. Cyclic voltammo-grams were recorded with an Ensman Instruments 400 potentiostat at a rate of 100 V s^{-1}.

The charge-retention characteristics of the triple-decker SAMs were measured using open circuit potential ampero-metry (OCPA) using instrumentation previously described.[34] Briefly, the experiment is performed as follows: (1) A potential is applied to the counter electrode to quantitatively oxidize the SAM. The potential is applied for ~20 ms and is ~100 mV above the formal potential for the oxidation process. (2) The counter electrode is disconnected from the potentiostat for a time period (τ). (3) During this time, the applied potential is changed to match the empirically determined open circuit potential (OCP) (which is ~125 mV *vs.* Ag/Ag$^+$ for the triple-decker SAMs). (4) The counter electrode is reconnected at the OCP and the reductive current is monitored. The magnitude of the resulting current is directly proportional to the number of molecules that remain oxidized while the electrode is dis-connected from the applied potential. (5) Charge retention is measured by successively changing the disconnect time (τ_1, τ_2, …) up to a point where essentially all of the molecules that were initially oxidized have decayed back to the neutral state during the time the electrode was disconnected.

Acknowledgements

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